CHEMISTRY

QUALITATIVE CHEMICAL
ANALYSIS

AN INTRODUCTION TO

THE SCIENCE AND PRACTICE OF

QUALITATIVE CHEMICAL ANALYSIS

INORGANIC

BY

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PREFACE

THE principal aim of this volume is to guide the student towards the attainment of systematic work in his qualitative analysis—to help him to learn a sound method rather than to fill his mind with innumerable isolated reactions.

For teaching the *method* of work, it is not only unnecessary but undesirable to attempt to include either all classes of compounds, or all the reactions of those that are considered. The selection made is that which long experience has shown to be the best for the purpose, and at the same time it includes all the more commonly occurring inorganic substances.

The reactions described are not only those utilised in the tabulated method given, but sufficient for the more advanced student to avail himself of in devising other methods in specific cases that can be advantageously treated in a special or different manner. A perfect system is an elastic one that may be adapted to various circumstances, and the student is encouraged to consider the tables given as guides rather than rigid rules, when he has had a little experience and can judge for himself.

There is a great deal more given in the book than it would be desirable for a student to actually confirm for himself while going over the reactions for the first time. Those parts that he should experimentally verify as far as he can before beginning any separations are indicated by asterisks, which signify that he should confirm for himself the statements in the paragraph so marked until he comes to the asterisk. Doubtless some teachers will differ from

the author as to the expediency of including or excluding certain parts at this stage of the work. But those who differ most will probably agree that it is an assistance to have some parts distinguished in this manner, rather than that the selection should be left entirely undone.

The author finds that a student who masters a method such as is herein set forth, understands the principles of analysis, and can easily extend his work to other substances, classifying them on similar lines. He has in fact learned the science or foundations of the subject, and, at the same time, had considerable opportunity for exercise in the practice of it. The extension of his practice follows naturally and also systematically when new substances are presented to him with their properties.

The numbering of the groups of the metallic radicals is the same as has been usual in this country, and is now so well known and commonly used that, although the author does not consider it the best, he believes that a change would lead to more confusion than benefit. And as the numbering is a mere matter of convenience, being of no importance whatever from a scientific or systematic point of view, the discrepancies in it in no way interfere with the teaching of the subject.

A special endeavour has been made to arrange the tabulated matter as clearly as possible. This part of the volume has been printed on parchmentised paper, so that if anything is spilled on to the book as it lies open at any of the tables, the result will not be so disastrous as it otherwise might be. It is hoped too that the greater width of these pages will serve to protect the other part of the book in case of accident.

The author desires to acknowledge with his best thanks his indebtedness to Professor Tilden for many valuable suggestions, chiefly with regard to nomenclature.

CONTENTS

THE SCIENCE AND PRACTICE OF QUALITATIVE ANALYSIS

THE word *analysis* signifies the act of pulling to pieces; but in chemistry it is synonymous with *examination*, and this is often the preferable word to use. Some compounds, such as mercuric oxide, can be actually separated into their constituents by simple means; but if a piece of pure zinc or copper is given for analysis, it is obvious that, as these are elements, the only kind of chemical change that they can be subjected to is the addition of some other matter to them; they cannot be chemically pulled to pieces because they consist of only one kind of matter.

Chemical analysis is called *qualitative* when its aim is to discover the quality or character of the constituents of any thing—in short, what the thing is from a chemical point of view; and it is *quantitative* when it is applied to the estimation of the quantity or proportion of those constituents. As any thing or material that can be got hold of can be subjected to analysis, it is impossible to have a complete treatise on the subject. The present work does not seek to approach completeness, but rather to help the student to learn, within comparatively narrow limits, a system or method perfectly serviceable within these limits,

and yet of such a character that it will serve by suitable expansion and development for any case with which he may afterwards have to deal.

Science is exact knowledge systematically arranged, the skilful application of it is the practice, and the two should go hand in hand. But it is more easy as well as more useful and instructive for the student at first to limit the number of substances with which he has to deal, so long as he has a sufficient number to thoroughly illustrate the principles involved. On the other hand, there are some facts given in this book that may appear not to have a direct bearing upon the systematic course of work that is given. The assistance that they render will become more evident as the student increases his experience.

It is generally desirable to do qualitative examinations quickly and yet with certainty. The ability to do this can come only by practice; but the practice to be success-ful must be well directed. In qualitative analysis we aim at using as small an amount of the material being worked upon as will give decisive results, and, in preparing solutions, to keep their bulks as small as convenient. Operations such as boiling and filtering may then be more quickly performed, and the changes effected are more decisive. It requires more skill and is generally more tedious to work with quantities that are much larger or smaller than a cer-tain convenient amount, and it is therefore desirable that special attention be paid to the indications of quantity given.

The apparatus used must be proportioned to the scale upon which the operations are to be conducted. Large vessels are not wanted for such work as is here treated of; they are a temptation to work clumsily, and invariably lead to waste of time, if not to failure.

Test tubes may be six inches long and three-quarters of

an inch in diameter, and at no time should there be fewer than a dozen at hand. Some test tubes of a smaller size are convenient when it is necessary only to add a few drops of a reagent and notice the effect. The test tube stand is best if provided with pegs on which to drain the washed tubes. Test tube brushes should be so shaped that they will clean the whole of the inside of the tubes without incurring the risk of breaking them.

Porcelain dishes of three inches in diameter and with round bottoms will be wanted. They should be of the best kind and well glazed.

Flasks of about two ounces' capacity are better for general use than the large test tubes sometimes called "boiling tubes." A few of rather larger sizes may be provided; but they will rarely be wanted, except that one of about thirty ounces' capacity, and another rather smaller, may be fitted up as wash bottles, like the figure.

In making a wash bottle it is important to notice that the tube leading to the jet should extend as near to the bottom of the flask as is safe, and that the sharp edges of the tubes should, without exception, be removed by heating them in the Bunsen flame until they are rounded by fusion. In rounding the edges of the tubes the heating must not be so prolonged as to narrow the opening, and the bends of the tubes must be made so that there is no constriction or distortion.
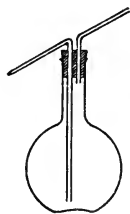
Funnels should be of two and two and a half inches in diameter, and the filter papers of three and a half and four and a half inches diameter.

A piece of platinum wire of medium thickness will be wanted, about six inches long, and a piece of platinum foil about two inches by one inch. The stouter the foil is the

longer it will last, if no accident happens to it. The foil should be kept smooth, and, if it gets wrinkled, it should be at once made smooth by rubbing it on a flat piece of glass with the handle of a pocket knife, or in some similar manner. For use, three of its edges are bent up to form a shallow tray.

A small square of cobalt glass should be provided, and it will be well to get it cut into four or six pieces, so that by the superposition of them a sufficient depth of colour may be obtained. To test the glass, a very bright yellow flame should be produced by melting some sodium carbonate into a small loop at the end of a platinum wire and holding this in the Bunsen flame. The colouration of the flame should be invisible through the blue glass, and the number of pieces that have to be superimposed to produce this effect should be noted.

The test papers of blue and red litmus should be well coloured, and are to be preferred if tinted on one side only, as extreme sensitiveness is not so much required as a decided reaction. It is often of no use to transform a red paper to a blue or a blue to a red when about to use it, if the kind wanted is not at hand, because the excess of alkali or acid, as the case may be, that remains impregnating the paper is likely to invalidate the test.

Watch glasses should be provided for putting substances on instead of using pieces of paper, but they are not suitable for performing reactions in.

Beakers, especially the larger sizes, are not often necessary for this work. The use of them tends to encourage too great an increase in the bulk of the solutions being dealt with.

A funnel stand also is but seldom required, as the funnels may be placed in the test tubes without further support.

There is no need to remark upon the other items of apparatus that are necessary. Bunsen burners with a rose and cone, a blow-pipe, porcelain crucibles, a tripod stand, wire gauze and a sand bath dish, a retort stand, &c., glass tubing and rod, india-rubber tubing, a thistle-headed funnel, a small retort, a pair of tongs, a pestle and mortar, a triangular and a round file, a pair of scissors, a spatula, cork borers, corks, and dusters should be provided. The dusters or cloths must be suitable for cleaning and drying glass, and one at least should be kept in fit condition for this purpose.

The apparatus and the bench should always be kept carefully clean; and apparatus, when washed, should be dried on the outside, if not all over, with a duster. Anything that is spilt should at once be cleaned away, because, if allowed to remain, it may lead to the contamination of some vessel or material; and the introduction of foreign matter is not unlikely to lead to perplexing reactions or erroneous results.

DIVISION OF THE BASIC (OR METALLIC) RADICALS INTO GROUPS

In separating the basic radicals from each other for the purpose of their identification, it is usual to first divide them into groups. If salts of all of those metals that are included in this course of study were present in the same solution, on the addition of hydrochloric acid, they would, to a greater or less extent, be converted into chlorides. But the chlorides of three of them, namely, silver, mercury in the mercurous condition, and lead, being insoluble (or nearly so) in such an aqueous liquid as would be produced, would separate out in the solid form. These three metals are therefore classed together as the first group.

If sulphuretted hydrogen was now passed into the acid solution, the compounds of mercury in the mercuric condition, bismuth, copper, cadmium, tin, arsenic, and antimony, and any lead compounds that remained, would yield the sulphides of these metals, which would separate as solids. These metals therefore constitute the second group.

If the liquid separated from these precipitates was made alkaline with ammonia and more sulphuretted hydrogen passed into it, the compounds of iron, zinc, manganese, nickel, and cobalt would yield the corresponding sulphides, while the salts of chromium and aluminium would yield

the hydrates of these metals. These sulphides and hydrates being all insoluble in the resulting liquid, would therefore separate in the solid condition. These metals constitute the third group.

The addition of ammonium carbonate to the remaining solution would convert the metals of the barium, strontium, and calcium salts into their carbonates, which are insoluble in the alkaline liquid. These metals are classed together as the fourth group.

The salts of magnesium, potassium, and sodium remain in solution, and these metals are spoken of as the fifth group. The reactions of ammonium compounds are generally studied in connection with this group because of the close relationship that exists between the compounds of potassium, sodium, and ammonium.

The following table shows the classification at a glance:—

Group 1.	Group 2.	Group 3.	Group 4.	Group 5.
Silver Mercury (Hg') Lead	Mercury (Hg'') Lead Bismuth Copper Cadmium Tin Arsenic Antimony	Iron Chromium Aluminium Zinc Manganese Nickel Cobalt	Barium Strontium Calcium	Magnesium Potassium Sodium

It should be understood that this division is not the only one possible, and that the numbers assigned to the groups are given to them only for the sake of convenience. Some chemists use different numbers, and others prefer

descriptive names, calling Group 4, for example, the alkaline earthy group.

In studying the reactions of these metals in their compounds, it is convenient to begin with the fifth group and proceed backwards, because the complexity and variety of the changes that are possible from an analytical point of view are least in the fifth group and greatest in the first and second.

It may be remarked here that, although in some cases the properties or reactions of the metals as such are given, in by far the greater number of cases it is not the reactions of the *metals* that are considered, but those reactions of their compounds that evidently are the result of the presence of the metal in them. It is the basic (or metallic) radicals of compounds that are dealt with, though sometimes for convenience they may be referred to as metals.

It is necessary for the student to take notes of the work that he does. In the experimental confirmation of the reactions, the notes may with advantage take the form of the following specimen for potassium :—

METHOD OF ENTERING NOTES

Potassium (used KCl).

Heated on a platinum wire—the flame was coloured violet.

Reactions in solution—

$$2KCl + PtCl_4 = 2KCl, PtCl_4$$
<div style="text-align:center">yellow cryst. ppt.</div>

$$KCl + C_4H_6O_6 = C_4KH_5O_6 + HCl$$
<div style="text-align:center">white cryst. ppt.</div>
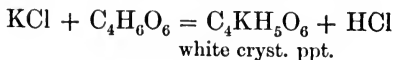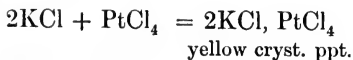
The equation that expresses the change for each operation is given, and a short description of the characteristic product is written under it. If an equation cannot be given, as in the first reaction, the operation and its result are stated in words as concisely as possible. To this may be added any fact of special importance, as, for example, in this case that the solution of the potassium salt must be concentrated, or that otherwise the precipitates will not separate. It is a mistake to endeavour to set down in the note-book all the details given in the text-book.

In confirming the reactions given, it is generally advantageous for the student to study the whole of the text, but to do only what is given in each paragraph before the asterisk. If all the statements in a paragraph are to be practically verified, the asterisk is put at the end; and, if there is no asterisk, the paragraph is to be studied without practical experiment. To confirm for himself every statement made as to the solubility and the other properties of precipitates that are not at once obvious would require more time than most students are able to devote to this part of their work.

THE BASIC (OR METALLIC) RADICALS OF GROUP V.

Potassium

Use potassium chloride (KCl). The compound that is directed here and in subsequent cases to be used is merely that compound that is considered to best illustrate the changes described, and the least likely to cause other changes that might complicate or render less obvious the effects to be studied.

Potassium compounds when volatilised in the non-luminous flame colour the flame violet. Take a straight-ended platinum wire, heat the end of it in the flame until the flame is no longer coloured by it. Moisten the end of the wire when it is cold by touching it to the tongue, and pick up on the very extremity a few specks of the finely-powdered salt. Slowly introduce the wire into the lower part of the flame, and the colour will be seen. Then make a small loop at the end of the wire, heat it, and while red hot touch a small fragment of a crystal of potassium nitrate that it may adhere. Carefully melt the nitrate into the loop, and then hold it in the flame. The compounds produced by heating the nitrate are more volatile than the chloride, and this salt is generally purer, so that the violet colouration is stronger and probably less mixed with yellow from the presence of a minute proportion of sodium

compounds.* Potassium compounds that are less volatile obviously would produce a less strong colouration.

Sodium compounds, if present in sufficient quantity, entirely hide this colouration because of the strong yellow colour they impart to the flame. By viewing the flame through a sufficient thickness of cobalt glass, the yellow is completely absorbed and the colour due to potassium appears as a reddish violet. A solution of indigo has a similar effect, and it is commonly used in a tapering bottle, or " indigo prism," so that a suitably thick layer may be selected.

Platinic chloride ($PtCl_4$) added to potassium salts in concentrated solutions gives a heavy bright yellow crystalline precipitate of potassium platinic chloride ($2KCl, PtCl_4$). If the solution is too weak and gives no precipitate, it should be concentrated by evaporation.* To test for a small quantity of potassium, the solution may be evaporated just to dryness after adding the platinic chloride, and the residue treated with alcohol; the potassium platinic chloride will then be left insoluble.

Tartaric acid ($C_4H_6O_6$) gives a white crystalline precipitate of hydrogen potassium tartrate ($C_4KH_5O_6$). The solution must not be weak. In any case the precipitate will probably not begin to form at once, and a vigorous shaking will promote its separation.*

There are other salts of potassium besides potassium platinic chloride and hydrogen potassium tartrate that are sufficiently insoluble in water (or alcohol) to serve for the detection of potassium. Among them are the silicofluoride ($2KF,SiF_4$), the perchlorate ($KClO_4$), and the picrate ($C_6H_2(NO_2)_3OK$). Of these the last will probably be found the most useful. A saturated solution in water of picric acid should be employed, and added in excess to the concentrated solution to be tested. Ammonium salts

must be absent. If no precipitate is produced, more picric acid should be added, and the mixture well shaken.

Sodium

Use sodium carbonate (Na_2CO_3) or sodium chloride (NaCl).

Sodium compounds, when heated on a platinum wire in the lower part of a non-luminous flame, colour the flame luminously yellow.* If the amount of sodium compound is appreciable, the flame will be very bright for at least a short time. A feeble or non-luminous yellow colour indicates, if sodium at all, a quantity that is negligible so far as the student is concerned at this stage of his work. Sodium may be met with, as in some minerals, in an almost non-volatile condition, then of course this test is not applicable.

Potassium pyro-antimonate ($K_2H_2Sb_2O_7$)[1] gives with neutral or slightly alkaline solutions of sodium salts a white crystalline precipitate of sodium pyro-antimonate ($Na_2H_2Sb_2O_7$). This reagent, however, is rarely used, and the getting of a residue after the other metallic radicals are removed (except perhaps magnesium and potassium) which gives a bright yellow flame, is invariably relied upon for proving the presence of sodium.

Ammonium

Use ammonium chloride (NH_4Cl).

Ammonium compounds, when heated in a dry test tube, always yield volatile products, and if the acid is volatile a sublimate is produced. Ammonium chloride is decomposed (or dissociated) into ammonia and hydrochloric acid; and

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[1] This salt is commonly called the metantimonate; but as it is analogous in its formula to the pyrophosphates, and not to the metaphosphates, the name given above is preferable.

this can be readily proved by putting a piece of red litmus paper in the upper part of the tube before beginning to heat it. The paper will be turned blue; and, after letting the tube cool for a few seconds, if the litmus paper is allowed to fall to the bottom of the tube, it will be changed to a full red. But the greater part of the ammonia and hydrochloric acid recombine and settle as solid ammonium chloride on the cooler parts of the tube.* Ammonium nitrate decomposes chiefly into nitrous oxide gas and water. Ammonium sulphate is also broken up by heat, giving water, nitrogen, ammonia and sulphurous anhydride, the last two gases partially combining to form a white sublimate. Ammonium phosphate gives off ammonia and water; the phosphoric acid is not volatile.

Ammonium salts, when ground in a mortar with an alkali or other analogous substance, especially if the mixture is moistened, evolve ammonia. Soda lime and a drop or two of water, or slaked lime and a drop or two of caustic soda solution may be used. The ammonia is detected by its unmistakable odour, or, if in small quantity, by its alkaline action upon red litmus paper.* The litmus paper may be placed, wet, on the under side of a clock glass with which the mortar is then covered. Or it may be put on the bottom of a beaker that is small enough to stand in the mortar that contains the mixture. The arrangement should be left for a few minutes to see if any change takes place. Obviously ammonia will be evolved from ammonium salts when they are mixed with an alkali and the mixture or solution is *heated*. This method is not to be recommended, as some organic substances that contain nitrogen would give off ammonia under the same circumstances, and it has no advantage over the other.

Platinic chloride ($PtCl_4$) and *tartaric acid* ($C_4H_6O_6$) behave with ammonium salts as with potassium salts,

except that the precipitate in each case ($2NH_4Cl,PtCl_4$, and $C_4(NH_4)H_5O_6$) is more soluble, and therefore comes more slowly, unless the solutions are more concentrated.*

Nessler's reagent, potassium mercuric iodide in solution with an excess of caustic potash ($2KI,HgI_2$), when added to water that contains even only a mere trace of ammonia either free or in combination, gives a brown precipitate, or a brown colour if the quantity of ammonia is exceedingly minute, due to the formation of mercuric ammonium iodide (NHg_2I). This reagent is not suitable for ordinary analytical operations, it is used almost exclusively in searching for and estimating the minute amounts of ammonia that occur in natural or purified waters.

Magnesium

Use magnesium sulphate ($MgSO_4, 7H_2O$)[1] or magnesium chloride ($MgCl_2,6H_2O$).

Magnesium salts do not colour the flame. Those which, when heated on charcoal leave a residue of oxide, such as the chloride or carbonate, give a pink residue if after ignition a drop of a solution of cobalt nitrate is put on the residue and it is heated again.* This test however is of very little value, for it rarely succeeds unless the residue after the first ignition is the pure oxide, and at its best the colour is not very marked.

Ammonia (AmOH), when added to the solution of a magnesium salt, gives a white bulky precipitate of magnesium hydrate ($Mg(OH)_2$)* ; but the precipitation is only partial because of the formation of the ammonium salt, which has a solvent action on magnesium hydrate.

If a sufficient quantity of ammonium chloride or sul-

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[1] In writing the equations, the water of crystallisation in this and all subsequent cases may be omitted.

phate is added to the solution first, the addition of ammonia produces no precipitate.* Magnesium hydrate even after precipitation is readily redissolved by the addition of an ammonium salt. In the presence of both ammonia and an ammonium salt, it depends upon the relative quantity of each whether magnesium hydrate is precipitated or not. The more of either that is present the more is required of the other to produce its own characteristic effect. By adding ammonia a precipitate is produced. Adding ammonium chloride effects its solution. More ammonia again gives a precipitate, and further ammonium chloride dissolves it. This alternate precipitation and solution may be performed several times in the same solution by adding the two reagents alternately.

The *hydrates* of potassium, sodium, barium, or calcium precipitate magnesium hydrate; potassium and sodium *carbonates*, especially on heating, precipitate basic carbonates of magnesia; ammonium carbonate gives a slight precipitate on boiling; but all these precipitates are soluble in ammonium salts, and the presence of ammonium salts prevents their formation.

Hydrogen disodium phosphate (HNa_2PO_4) gives a white precipitate of hydrogen magnesium phosphate ($HMgPO_4$). In the presence of ammonia, the addition of which should be preceded by ammonium chloride to prevent the precipitation of the hydrate, ammonium magnesium phosphate ($AmMgPO_4$) is formed.* If the solution is rather dilute the precipitate will appear slowly, and will be distinctly crystalline. In stronger solutions it comes at once, and its crystalline character is not obvious. The application of hydrogen disodium phosphate in the presence of ammonia is the test that is invariably used in seeking for magnesium.

COMPARATIVE REMARKS ON THE BASIC (OR METALLIC) RADICALS OF GROUP V.

MAGNESIUM, POTASSIUM, AND SODIUM (INCLUDING AMMONIUM)

Magnesium is characterised by the insolubility of its phosphate in water or in solutions containing ammonia, and of its oxide in water, though this latter property is not often utilised in qualitative analysis. Ammonium compounds are markedly different from compounds of potassium, sodium, and magnesium, in the volatility of the ammonia when liberated either by simple heating or by the action of an alkali. Potassium and ammonium compounds are similar in their behaviour with platinum chloride and tartaric acid; but if by previous heating the ammonia is driven off, then potassium alone of the members of this group responds to these reagents.

Separation. It is not as a rule necessary to separate (or get rid of) magnesium before testing for potassium and sodium, and in the method of detecting the metallic radicals of this group given in the table at page 177, this is not done. It is however possible by (1) evaporating to dryness the solution that contains the compounds of the metals and igniting to get rid of ammonium compounds; (2) treating the residue with water, when a part of the magnesium may remain as oxide, and adding sufficient barium hydrate to precipitate the rest of the magnesium; (3) adding ammonium carbonate to the filtered solution to get rid of the barium; (4) and after filtering again evaporating to dryness and igniting to get rid of the ammonium salts. The residue so obtained contains no other basic radicals than the potassium and sodium origin-

ally present.   It is necessary to get rid of the ammonium compounds before precipitating the magnesium with barium hydrate, because the resulting magnesium hydrate is soluble in ammonium salts, and therefore cannot be precipitated in their presence.

THE BASIC (OR METALLIC) RADICALS OF GROUP IV.

Barium

Use barium chloride ($BaCl_2, 2H_2O$).

Many barium compounds, when heated on a platinum wire in the lower part of a non-luminous flame, colour the flame yellowish green.* As the compounds of the metals of this group are as a rule less volatile than the compounds of potassium and sodium, it is advantageous, when seeking to get their characteristic flame colourations, to use as thin a wire as possible that it may be more intensely heated. And as the chlorides are specially favourable compounds for this test, the colour will often be rendered more intense, especially after it has begun to fade, by dipping the wire into concentrated hydrochloric acid and trying the reaction again.

Ammonium carbonate (Am_2CO_3) gives from solutions of barium salts a white precipitate of barium carbonate ($BaCO_3$)* which is easily soluble in dilute acids. If an acid is present, some of the carbonic anhydride liberated combines with a part of the barium carbonate to form an acid carbonate that is soluble in water. Boiling will drive out the carbonic anhydride and complete the precipitation. Sodium and potassium carbonates produce the same precipitate.

Ammonia (AmOH) gives no precipitate.   *Potassium* or *sodium hydrate* (KOH or NaOH) precipitates barium hydrate $(Ba(OH)_2)$ from concentrated solutions of barium salts; but the precipitate dissolves readily on adding water. These caustic alkalies are rarely free from carbonates and sulphates; and these compounds, if present, give the carbonate and sulphate of barium, salts that will not dissolve on dilution.

Sulphuric acid (H_2SO_4) gives from even very dilute solutions a white precipitate of barium sulphate $(BaSO_4)$,* which is not appreciably affected by the addition of any acid or alkali to the liquid containing it.   Barium sulphate is slightly soluble in strong hydrochloric or nitric acid, in concentrated solutions of ammonium salts, and in the presence of some organic substances, such as alkaline citrates and gelatine.   It is soluble in hot concentrated sulphuric acid.

Potassium chromate (K_2CrO_4) gives a yellow precipitate of barium chromate $(BaCrO_4)$.   The precipitation is not appreciably affected by the presence of acetic acid, but the barium chromate dissolves readily in dilute hydrochloric or nitric acid.*

Hydrofluosilicic acid $(2HF,SiF_4)$ gives a white crystalline precipitate of barium silicofluoride (BaF_2,SiF_4), and the separation is rendered complete by the addition of an equal volume of alcohol.

Hydrogen disodium phosphate (HNa_2PO_4) gives a white precipitate of hydrogen barium phosphate $(HBaPO_4)$* which is soluble in acids, even acetic.

Ammonium oxalate $(Am_2C_2O_4)$ gives a white pulverulent precipitate of barium oxalate (BaC_2O_4)* which is soluble in dilute hydrochloric or nitric acid.   It is also soluble in acetic acid when freshly precipitated; but a crystalline precipitate of the acid oxalate soon begins to form.

Strontium

Use strontium chloride ($SrCl_2,6H_2O$).

Most strontium compounds, when heated on a platinum wire, colour the flame a fine and intense red. Hydrochloric acid will make the colour stronger when it has faded.*

Ammonium carbonate (Am_2CO_3) gives from solutions of strontium salts a white precipitate of strontium carbonate ($SrCO_3$)* easily soluble in dilute acids. The presence of carbonic acid leads to the formation of some acid carbonate which is soluble in water and decomposed on boiling.

The effects of ammonia, potassium and sodium hydrates, and potassium and sodium carbonates, on solutions of strontium salts are practically the same as upon solutions of barium salts.

Sulphuric acid (H_2SO_4) gives a white precipitate of strontium sulphate ($SrSO_4$)* which is not visibly affected by the subsequent addition of acids or alkalies. If the solution of the strontium salt is rather dilute the precipitate will form slowly. Strontium sulphate is much more soluble in water than barium sulphate. The precipitation of strontium sulphate is therefore incomplete to an extent that can be recognised, unless indeed alcohol is added to the solution.

Potassium chromate (K_2CrO_4) gives slowly, from neutral solutions, a yellow precipitate of strontium chromate ($SrCrO_4$). On warming, the precipitate separates copiously. It is soluble in dilute acids, even in acetic acid.*

Hydrofluosilicic acid ($2HF,SiF_4$) gives no precipitate with strontium salts, nor even on the addition of an equal bulk of alcohol unless the solution is concentrated.

Hydrogen disodium phosphate (HNa_2PO_4) gives a white

precipitate of hydrogen strontium phosphate ($HSrPO_4$)*
soluble in dilute acids, including acetic.

Ammonium oxalate ($Am_2C_2O_4$) gives a white precipitate
of strontium oxalate (SrC_2O_4)* which is soluble in hydro-
chloric or nitric acids, but very sparingly soluble in acetic
acid.

Calcium

Use calcium chloride ($CaCl_2,6H_2O$).

Many calcium compounds, when heated on a platinum
wire, colour the flame red. The use of hydrochloric acid
generally makes the colour more vivid. The colour given
by calcium compounds that are not too difficult to volati-
lise, such as the chloride, if free from sodium compounds,
is so bright a red that it is often mistaken for the colour
due to strontium. But the red given by calcium salts is
of a markedly more yellowish tint, and the difference may
be well shown by taking a little strontium chloride on one
wire and some calcium chloride on another, and bringing
them simultaneously into opposite sides of the same
flame.*

Ammonium carbonate (Am_2CO_3) gives from solutions of
calcium salts a white precipitate of calcium carbonate
($CaCO_3$)* which is easily soluble in dilute acids. The
precipitate is at first bulky, but on warming it at once
becomes compact, heavy, and crystalline. Free carbonic
acid produces the soluble acid carbonate, and therefore
prevents complete precipitation unless the liquid is
boiled.

The effects of ammonia, potassium and sodium hydrates
and their carbonates on solutions of calcium salts are
practically the same as with barium and strontium
compounds

Sulphuric acid (H_2SO_4) gives no precipitate unless the

solution is strong, then a bulky white precipitate of hydrated calcium sulphate ($CaSO_4$) separates.* In less strong solutions the sulphate may separate on standing; dilute solutions yield no precipitate. Calcium sulphate dissolves with fair ease on warming it in dilute hydrochloric acid. It is more soluble in a strong solution of ammonium sulphate on warming.

Potassium chromate (K_2CrO_4) gives only a slight precipitate with even strong solutions of calcium chloride and on warming, and the precipitate dissolves at once on adding a drop or two of acetic acid.*

Hydrofluosilicic acid ($2HF,SiF_4$) gives no precipitate with calcium salts.

Hydrogen disodium phosphate (HNa_2PO_4) gives a white precipitate of calcium phosphate ($Ca_3P_2O_8$)* which is soluble in dilute acids, including acetic.

Ammonium oxalate ($Am_2C_2O_4$) gives a white pulverulent precipitate of calcium oxalate (CaC_2O_4) even from very dilute solutions of calcium salts. The precipitate is practically unaffected by acetic acid, but dissolves readily in nitric or hydrochloric acid.*

GENERAL REMARKS ON ANALYTICAL REACTIONS

The student having now gained a little experience, this is a convenient place for a few remarks on analytical reactions in general. Students often ask whether they are expected to remember all the reactions that they give attention to, and the answer is—yes, but not individually. If there were no connection between the various chemical changes that are utilised for analytical purposes, if each were an isolated and distinct case, analytical chemistry would be mere empirical art and not a science.

When a chemical change takes place between two

substances that are brought together, there is a rearrangement of their constituents; and it is possible to trace this diagrammatically.   In every case a mental picture should be formed of the movements of the parts of the substances that react, and, if this is not at once clear, the formulæ should be set down on paper that the exact character of the change may be traced out.   When platinic chloride is brought into contact with potassium chloride in solution, the two salts combine to form potassium platinic chloride, and this is the only result of the change.   But the greater number of changes are not of this character.

If two salts that have different acid and basic radicals are brought together in solution, two other salts are formed by the basic radical of each combining with the acid radical of the other.   Taking for example barium chloride and potassium chromate; these, if mixed in solution, produce barium chromate and potassium chloride, and this may be illustrated either in words or in symbols, thus :—
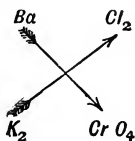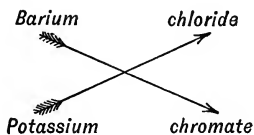
Or, it may be said that the two basic radicals, or the two acid radicals, change places to a certain extent.   This kind of change is called "double decomposition."   If either of the two new compounds is insoluble in the solution used, it separates in the solid condition and is technically called a "precipitate."   The word "precipitate" does not indicate that the solid substance formed will settle down to the bottom of the vessel; it may float to the upper part of the liquid, or remain suspended in it neither

floating nor sinking, and in all cases it is technically called a "precipitate."

If the beginner finds any difficulty in writing down the equations for his work, diagrams of the above kind will in most cases get rid of the difficulty. The name and formula of the substance taken, of the reagent added, and of the product to which special attention is directed, are given in the text; there ought then to be no trouble in finding the name and formula of the other product or products needed to complete the equation.

But these diagrams illustrate very much more than this. If it is desired to test for barium in a solution by the production of the characteristic precipitate of barium chromate, it is obvious that any soluble chromate may be used. Either ammonium or sodium chromate will serve as well as potassium chromate, the only difference being that ammonium or sodium chloride will be produced instead of potassium chloride, and neither of these chlorides interferes in any way.

In like manner instead of sulphuric acid for precipitating barium sulphate from a solution of barium chloride, sodium or potassium sulphate may be used. But if silver sulphate were employed there would then be two insoluble substances produced—silver chloride in addition to the barium sulphate—and the test for barium would be invalidated. It is always important to produce nothing that will interfere with the characteristics of the substance the appearance of which is to answer the question that it is sought to solve—in this case, whether barium is present or not in the solution.

It is possible therefore to vary the reagents used, and it is desirable eventually that the student shall know when and how it is advantageous to do this; but for the present he should adhere strictly to those that are named. They

are selected on various accounts. Some may be more easily obtainable than the alternative compounds, others may generally be purer, others are less likely to complicate the work by introducing undesirable constituents. The students should not at this stage of the work trouble himself much by seeking for reasons for the selection made.

In the reactions that have been given, the properties of each metallic radical have been grouped together, but it is necessary and very helpful to regard these reactions also by putting together the effects of the various reagents one at a time on the compounds of the different metals. It will be noticed for example that sodium phosphate precipitates the phosphates of the metals magnesium, barium, strontium and calcium, and by its action upon the salts of the metals of the groups yet to be considered, it also, as a rule, causes the precipitation of the phosphate of the metal. The general action therefore of sodium phosphate is to give as a precipitate the phosphate of the metal contained in the solution to which it is added. Similarly, the general effect of sodium carbonate is to precipitate the carbonate of the metal, potassium chromate to precipitate the chromate, and so on. This is a general principle, but a few apparent exceptions will be found.

It will of course always be understood that a precipitate is not formed unless the compound produced is insoluble under the existing conditions. Sodium phosphate when added to a solution of calcium chloride gives a precipitate of calcium phosphate. But all phosphates are soluble in hydrochloric acid. If therefore hydrochloric acid is first added to the solution and then sodium phosphate, no precipitate results, because the calcium phosphate that otherwise would be precipitated is soluble in the liquid.

Another matter that may be noticed here, and that is of

general applicability, is the reprecipitation of precipitates that have been dissolved in an acid, by the neutralisation of the acid. The phosphates and oxalates of barium, strontium and calcium are soluble in acids and reprecipitated on adding ammonia, while the carbonates of these metals are soluble in dilute acids and not reprecipitated on adding ammonia. A moment's thought will show that the oxalic and phosphoric acids remain in the liquid when the precipitate is dissolved, and one would expect therefore to reproduce the precipitate by neutralising the acid. But the carbonate effervesces when it is dissolved, and as the carbonic anhydride or the greater part of it passes away, the reproduction of the carbonate by adding ammonia is impossible.

COMPARATIVE REMARKS ON THE BASIC (OR METALLIC) RADICALS OF GROUP IV.

(BARIUM, STRONTIUM, AND CALCIUM)

Solutions of compounds of these metals yield precipitates with ammonium carbonate, and this is the reagent used to separate or test for the group as a whole. It should be added after ammonium chloride and ammonia that the solution may be alkaline, and that magnesium may not be precipitated as carbonate or hydrate, as it otherwise might be. Ammonium carbonate is the most convenient group reagent, because although sodium or potassium carbonate would give the same precipitates, the introduction of the alkali metals would interfere with the search for them in the filtrate. Sodium phosphate gives a precipitate with every member of this group, but it also precipitates magnesium phosphate. Sulphuric acid precipitates the sulphates of the three metals and does not give a precipitate with magnesium salts, but calcium

sulphate is precipitated so incompletely that this reagent would serve but poorly.

Barium is distinguished from strontium and calcium by the colour that its compounds give to the flame, and also by the insolubility of its chromate in acetic acid, the insolubility of its silicofluoride, the superior insolubility and greater stability of its sulphate, and the insolubility of its anhydrous chloride in alcohol.

Strontium is distinguished from calcium by the superior insolubility of its sulphate, by the insolubility of its sulphate in a hot concentrated solution of ammonium sulphate, and the insolubility of its anhydrous nitrate in alcohol.

The most sensitive reagent for calcium is ammonium oxalate. It will give a very obvious precipitate with many ordinary waters because of the lime they contain. The most sensitive reagent for barium is sulphuric acid.

It should be observed that in almost every case the reactions shown by strontium compounds are intermediate in character between those of barium and calcium compounds. This is especially noticeable in the insolubility of the sulphates, chromates, and oxalates, so far as the reactions are given above.

Separation. There are several methods by which these three metals may be analytically separated from each other. One is given in the table at page 177. Other serviceable methods are the following :—(1) Dissolve the precipitated carbonates in hydrochloric acid, evaporate the solution to dryness and very gently heat the remaining chlorides to get them dry, and then grind the residue with absolute alcohol. The chlorides of strontium and calcium dissolve, and the chloride of barium remains. The solution may be diluted with water, the carbonates of strontium and calcium precipitated with ammonium carbonate, the precipitate dissolved in dilute nitric acid, the solution

evaporated to dryness to get the dry nitrates, and these ground with absolute alcohol. The calcium nitrate dissolves, and the strontium nitrate remains. Each metal can then be further identified. (2) Precipitate the sulphates of the metals by means of dilute sulphuric acid and alcohol. The alcohol is necessary to precipitate the calcium sulphate. Then wash the precipitate and boil it for ten minutes with a solution of three parts of sulphate to one part of carbonate of potassium, then wash again. The strontium and calcium sulphates are changed into carbonates and may be dissolved in dilute acids, leaving the barium sulphate. The strontium and calcium sulphates may be again precipitated and then digested with a warm concentrated solution of ammonium sulphate to dissolve the calcium sulphate. Or the three sulphates may be first digested with a solution of ammonium sulphate to dissolve the calcium sulphate, and the residual barium and strontium sulphates separated as above. (3) Barium silicofluoride may be first precipitated with hydrofluosilicic acid and alcohol (a bulk equal to the solution). After filtering, sulphuric acid will precipitate the sulphates of strontium and calcium, and these may be separated as before.

A solution of calcium sulphate obviously will not precipitate calcium salts. But as strontium sulphate is less soluble, and barium sulphate still less soluble, it gives a precipitate with solutions of salts of both these metals, an immediate precipitate with barium salts, and a slowly forming precipitate with calcium salts. But a weaker solution of a barium salt would also yield a precipitate slowly, so that this method of work does not merit much confidence. It is, however, sometimes useful.

Before proceeding with the next group, the student should practice the separation and detection of the

metallic radicals of groups 4 and 5, by examining two or three solutions, each containing a selection of them by the methods given in the tables on p. 177. The notes of these analyses should be entered in tabular form after the manner of the following example :—

Exam. of a Solution for the Basic Radicals of Groups IV. and V.

Added AmCl, AmOH and Am_2CO_3 and warmed.

White ppt.	Sol.
Grp. 4 prest.	Grp. 5.

Exam. of Ppt. for Grp. IV.

Dissolved in dilute acetic acid, added K_2CrO_4.

Yellow ppt. dissolved in dilute HCl. added H_2SO_4. white ppt. Ba prest.	Sol. added Am_2SO_4 and let stand.	
	No ppt. Sr abst.	Sol. added $Am_2C_2O_4$. white ppt. Ca prest.

Exam. of Sol. for Group V.

Divided into two parts.

1. Added HNa_2PO_4. no ppt. Mg. abst.	2. Evapd. to dryness, ignited. Heated on platinum wire. A violet flame. K prest. Na abst. Dissolved in H_2O, added $PtCl_4$, evapd. just to dryness, added alcohol and a little H_2O, a heavy yellow ppt. remains. K prest.

Found Ba . Ca . K.

With regard to these and other notes it should be observed particularly (1) That the tabular form is strictly adhered to ; it saves time and makes the notes more clear, besides having other advantages. (2) That any intelligible contraction may be used. (3) That there is a clear and inclusive title to the exercise, and also clear titles to each section as necessary ; the titles show the aim of the work. (4) That the result of the work is set forth clearly and concisely at the end. It is not necessary to say that the liquid was filtered at the various stages, because the putting of the precipitate and solution in separate columns shows that they were separated—*how* they were separated is a mere matter of convenience.

Notes should always be full but concise, and above all things clear.

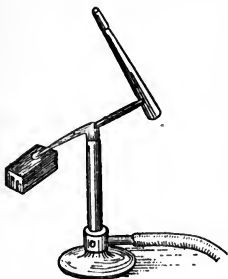# THE BASIC (OR METALLIC) RADICALS OF GROUP III., SECTION B

Zinc

Use zinc sulphate ($ZnSO_4,7H_2O$).

Zinc compounds when heated on charcoal with an alkaline flux such as fusion mixture are reduced to the metallic state, but the metal when reduced is in the vaporous condition because of its easy volatility. As it escapes through the flame it is reoxidised by the air, and a part of it settles upon the surrounding cooler parts of the charcoal as an incrustation, which is yellow when hot and white when cold. The zinc cannot by this method be obtained in the metallic condition.

In performing this experiment it will be better to use zinc oxide or zinc carbonate. A small quantity should be mixed with five or six times its bulk of fusion mixture, and then placed on a shallow circular depression rather less than half an inch in diameter scraped out in the side of a piece of charcoal. The blocks of artificial charcoal are preferable to wood charcoal prepared in the usual way. The charcoal and blowpipe should be held in the position shown in the figure. The Bunsen burner should have its air-holes closed, and the flame should be lowered until it is about two inches in height; the flame is too high unless almost the whole of it is carried in the direction of the air

issuing from the nozzle of the blowpipe.   No special
"blowpipe jet" is wanted for the burner.*

The blowpipe flame can be made to produce
either reduction or oxidation, and it is preferable to
vary the flame accordingly.   For
reduction, the nozzle of the blow-
pipe should be held just outside
the flame, and the blast should be
so gentle that while it carries the
flame over it does not destroy the
luminosity or whiteness of it.   The
substance to be reduced should be
heated within the luminous point of
the flame, so that it is covered by the
flame and access of air to it is prevented.   For oxidation,
the blowpipe nozzle should be introduced *into* the flame
about one-fourth of its diameter, and the blast should be
rather stronger than before, but not so strong as to give
a ragged flame or produce a hissing sound.   This flame is
not luminous but blue, and the substance to be oxidised
should be heated at the very extremity of it, so that while
it is being heated the air may be in contact with it, and
produce the required change.   Reduction is effected by
the unburned material of the flame itself, but oxidation is
done by the air, the flame simply heating the material.

Any zinc compound that when heated leaves the oxide
(such as the oxide itself or the carbonate), gives a green
mass if after heating it on charcoal in the outer (or oxi-
dising) flame and allowing it to cool, it is moistened with a
solution of cobalt nitrate, and again heated in the outer
flame.   The incrustation obtained as stated above, if in
sufficient quantity, would show this reaction.

Ammonium sulphide (Am$_2$S) gives with solutions of zinc
salts a white precipitate of zinc sulphide (ZnS).*   The

precipitate is not soluble in excess of the reagent nor in alkalies, but it is easily soluble in dilute hydrochloric, nitric or sulphuric acids.   It is not soluble in acetic acid.

Sulphuretted hydrogen (H_2S) gives the same precipitate from alkaline solutions of zinc salts, and also from a solution of zinc sulphate in spite of the sulphuric acid that is liberated by the reaction; but the addition of a little free mineral acid prevents the precipitation altogether.   The presence of free acetic acid does not prevent the precipitation of zinc sulphide.

Sodium hydrate (NaOH) gives a white precipitate of zinc hydrate ($Zn(OH)_2$) readily soluble on adding more of the reagent.*   The hydrate is reprecipitated from this solution by boiling it, unless it is too concentrated.   Zinc and chromium hydrates when precipitated together with caustic soda, form a compound insoluble in excess of the alkali.

Ammonia (NH_4OH) gives the same precipitate and also redissolves it on adding an excess.*   On boiling, the hydrate is reprecipitated.   Ammonium salts prevent the precipitation.

Sodium carbonate (Na_2CO_3) gives a white precipitate of a basic carbonate of zinc ($2ZnCO_3, 3Zn(OH)_2, 4H_2O$),[1] carbonic anhydride escaping.*   Ammonium salts if present in large quantity prevent the precipitation.

Ammonium carbonate (Am_2CO_3) gives the same precipitate, soluble in excess.

Manganese

Use manganous sulphate ($MnSO_4, 4H_2O$) or manganous chloride ($MnCl_2, 4H_2O$).

[1] The precipitate is probably not always exactly of the composition here represented.

To make a borax bead, the extreme end of the platinum wire should be bent round the point of a lead pencil, or something of the same kind, into a small loop, not so large but that it can be completely covered by the blowpipe flame. The loop is heated and plunged into powdered borax, and this is repeated until sufficient borax has accumulated to form when melted a bead of convenient size. A very small speck of the material to be examined is made to adhere by touching it with the hot and soft bead, and it is heated in the outer flame (as described in the section on Zinc) until the substance has dissolved. More substance may be taken, or a part of the bead may be jerked off and more borax added, according to whether the colour is not deep enough or is too dark.

Borax, $Na_2B_4O_7$, may be supposed to consist of sodium meta-borate and boric anhydride, $2NaBO_2 + B_2O_3$. This anhydride by combining with the oxide of a dyad metal would form a borate, thus for a metaborate, $B_2O_3 + M''O = M''B_2O_4$. There doubtless is in a borax bead a double borate of the metal introduced and sodium, together with a large excess of borax; but the exact nature of the compounds formed is not known, and the above must be taken as only illustrating the general character of the changes that take place.

Microcosmic salt may be used instead of borax. The bead in this case consists of sodium meta-phosphate produced by the decomposition of the salt on ignition, thus:—

$$HNa(NH_4)PO_4 = NaPO_3 + NH_3 + H_2O.$$

And this sodium metaphosphate with the oxide of a diad metal might yield a double orthophosphate of sodium and the metal, thus:—

$$NaPO_3 + M''O = NaM''PO_4,$$
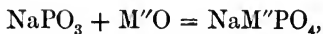
or a double pyrophosphate, thus :—

$$2NaPO_3 + M''O = Na_2M''P_2O_7.$$
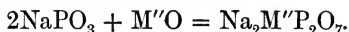
The double phosphate is of course diluted with a large excess of sodium metaphosphate. As in the case of borax the equations here given must be accepted as illustrating the general nature of the reaction only. The formulæ of the compounds produced are not known, but it appears probable that in most cases the products are more complicated than shown above.

Manganese compounds heated in a borax bead give a reddish brown bead inclining to violet when hot in the outer flame, and a quite colourless bead in the inner flame.* Microcosmic salt gives similar results.

A very characteristic reaction for manganese is the green colour produced when even the smallest quantity of one of its compounds is heated with fusion mixture and a little potassium nitrate. The reaction is conveniently done on platinum foil.* The fused mass becomes opaque as it cools. The green colour is due to the formation of an alkaline manganate (K_2MnO_4). This reaction is very delicate and is not interfered with by the presence of other substances.

Manganous chloride when heated on a platinum wire readily volatilises and colours the nonluminous flame green,* a colour similar to that imparted to the flame by barium salts. Other manganese compounds, if heated on the wire and then moistened with strong hydrochloric acid, give the same colouration to the flame when reheated.

Ammonium sulphide (Am$_2$S) gives with solutions of manganous salts a pink or salmon coloured precipitate of manganous sulphide (MnS).* The precipitate does not dissolve in excess of the reagent, but it is easily soluble in dilute acids, including acetic.

Sulphuretted hydrogen (H_2S) gives the same precipitate from alkaline solutions, but free acetic acid prevents the precipitation.

Sodium hydrate (NaOH) gives a white precipitate of manganous hydrate ($Mn(OH)_2$). On exposure to the air this precipitate changes gradually to a sepia brown colour,* absorbing oxygen to form a hydrate of the sesquioxide (Mn_2O_3).

Ammonia (AmOH) gives the same precipitate. In the presence of sufficient ammonium chloride ammonia gives no precipitate,* therefore the simple addition of ammonia to a solution of a manganese salt does not give complete precipitation, because of the ammonium salt produced. If both ammonium chloride and ammonia are present it depends upon which is in excess as to whether a precipitate is produced or not. As the quantity of either is increased so more of the other is necessary to produce its characteristic effect. By adding ammonia and ammonium chloride alternately, the precipitate may be produced and dissolved alternately a few times.

The ammoniacal solution containing manganese absorbs oxygen, by exposure to the air, with formation of the brown hydrated sesquioxide,* and as this is not soluble in ammonium salts it separates as a precipitate as soon as it is produced.

Sodium carbonate (Na_2CO_3) gives a white precipitate of manganous carbonate ($MnCO_3$),* which turns brown through oxidation on exposure to the air, but very much more slowly than manganous hydrate.

Manganese furnishes other more highly oxidised compounds than those mentioned. The oxides set down in the following series are known either in the isolated condition or in combination:—

$$MnO, \quad Mn_3O_4, \quad Mn_2O_3, \quad MnO_2, \quad MnO_3, \quad Mn_2O_7.$$
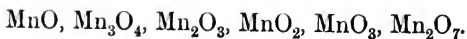
The first corresponds to the hydrate produced by precipitation from manganous salts. The second (Mn_3O_4) is the oxide produced on ignition in air at a high temperature of any oxide or of any manganese compound that contains only volatile matter other than the manganese, as, for example, manganous carbonate. The third (Mn_2O_3) is produced in the hydrated form by aerial oxidation of moist manganous hydrate. The fourth (MnO_2) can be produced by the oxidation of manganous compounds by means of chlorine or bromine in suitable aqueous solutions. It is black, and occurs as the common mineral pyrolusite. The second and third oxides also occur as minerals. The fifth (MnO_3) is the oxide, or anhydride, corresponding to the manganates, and the last (Mn_2O_7) is the anhydride corresponding to the permanganates.

By simply heating a manganese compound with fusion mixture in the presence of air, green manganates will be formed, but it is usual on the small scale to add an oxidising agent such as potassium nitrate, to hasten the reaction. An alkaline manganate when dissolved in water has a tendency for one part of it to oxidise another part with formation of a permanganate and separation of the hydrated dioxide, especially when heated, thus:—

$$3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 4KOH.$$

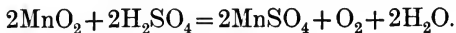This change is facilitated by the addition of a little acid. It can be traced by the change of the green colour of the manganate into the purple colour of the permanganate and the separation of the black precipitate.

All manganese oxides and all manganates and permanganates, when heated with strong hydrochloric or sulphuric acid, furnish manganous chloride or sulphate as the case may be, and with all these, except the lowest oxide,

chlorine or oxygen is given off. Thus potassium permanganate and hydrochloric acid give :—

$$K_2Mn_2O_8 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O.$$
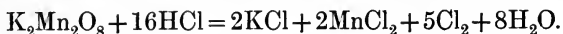
The black oxide of manganese and sulphuric acid give :—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O.$$

Potassium permanganate in dilute solution with sulphuric acid is very stable, but it is at once reduced by many substances susceptible of oxidation. Ferrous salts are converted into ferric salts by it, and a solution of potassium permanganate is often used as a measure of the quantity of ferrous salt present. The rich purple colour of the permanganate entirely disappears when it is added to an excess of a ferrous salt (or other oxidisable substance), and by adding a permanganate solution until a drop is not decolourised but imparts a red tint to the solution, the amount of ferrous salt present can be calculated if the bulk used and the strength of the permanganate solution used are known. Its strength can be estimated by adding it in measured quantity to a known amount of a ferrous compound in solution until the completion of the oxidation is shown by the permanent pink colour being produced.

It should be observed that the oxidation of manganese compounds is favoured by the presence of alkalies and retarded by the presence of acids. Under suitable conditions acids undo any oxidation that may have taken place, reproducing manganous salts.

Nickel

Use nickel sulphate ($NiSO_4,7H_2O$).

Heated on charcoal with fusion mixture, nickel salts are reduced, and a grey, slightly magnetic powder results. The metallic powder is mixed with the flux, and probably

will be partly carried into the pores of the charcoal. The part of the charcoal upon which the operation has been effected should be scraped out, ground with water in a small mortar, and the liquid, which dissolves the flux and floats away the particles of charcoal that have not got thoroughly soaked, poured away. The heavy metallic powder remains at the bottom, and, if desired, the remaining charcoal can be got rid of by running water over it. This test is of little value when one has other than simple blowpipe apparatus to work with.

Nickel compounds heated in a borax bead give in the outer flame a reddish-brown bead, which inclines to violet when hot. In the inner flame the bead loses its colour and becomes turbid from the particles of the metal that are precipitated.* If the bead is held in one position and kept hot, these particles will sink to the lowest part and leave the bead colourless.

Ammonium sulphide (Am$_2$S) gives from solutions of nickel compounds a black precipitate of nickel sulphide (NiS).* The precipitate dissolves perceptibly in excess of ammonium sulphide if it is yellow or contains free ammonia, forming a brown solution. The nickel sulphide so dissolved is precipitated on boiling, or more rapidly by adding acetic acid to decompose the ammonium sulphide. Nickel sulphide is practically insoluble in dilute hydrochloric acid, though the presence of the dilute acid prevents its precipitation. It is readily attached by aqua regia or by chlorine in aqueous liquids.

Sulphuretted hydrogen (H$_2$S) precipitates nickel sulphide completely in the presence of an alkaline acetate, as then only acetic acid is liberated, and this does not prevent precipitation.

Sodium hydrate (NaOH) gives a light green precipitate of nickel hydrate (Ni(OH)$_2$)* which is not dissolved on

adding excess of the reagent, and does not change by exposure to the air. The precipitate is soluble in ammonia or carbonate of ammonia.

Ammonia (AmOH) gives a slight precipitate that is similar in appearance and probably in composition to that produced by sodium hydrate, which readily dissolves on adding more ammonia, forming a blue solution. No precipitate is produced in the presence of ammonium chloride.*

Sodium carbonate (Na_2CO_3) gives a light green precipitate of a basic carbonate,* the composition of which varies according to the circumstances under which it is produced.

Ammonium carbonate (Am_2CO_3) gives a similar precipitate, which dissolves in excess of the reagent forming a blue solution.*

For other reactions of nickel, see the section headed Comparative Remarks that follows Cobalt.

Cobalt

Use cobalt chloride ($CoCl_2,6H_2O$), or cobalt nitrate ($Co(NO_3)_2,6H_2O$).

Heated on charcoal with fusion mixture a grey slightly magnetic powder results, which may be separated as described under Nickel.

Cobalt compounds impart to a borax bead a fine blue colour unalterable in either the inner or outer flame.* This reaction is characteristic and also delicate, so that it will often show in spite of the presence of other substances that colour the bead. With microcosmic salt a similar result is obtained, but it is stated not to be so delicate a reaction.

Ammonium sulphide (Am_2S) gives with solutions of cobalt compounds a black precipitate of cobalt sulphide

(CoS),* which is not soluble in the reagent, as nickel sulphide is. It resembles nickel sulphide in being practically insoluble in dilute hydrochloric acid, and readily attacked and dissolved by aqua regia or aqueous liquids containing free chlorine.

Sulphuretted hydrogen (H_2S) precipitates cobalt sulphide completely from solutions containing an alkaline acetate, as acetic acid does not prevent its precipitation, though dilute mineral acids do.

Sodium hydrate (NaOH) gives a very rich blue precipitate of a basic salt. On exposure to the air this precipitate oxidises, changing to a green and eventually to a dark brown colour, especially on heating. If the solutions are hot, or by heating after the blue precipitate has been obtained if oxidation does not take place, or by allowing the blue precipitate to stand in the cold in excess of caustic soda, a pale red precipitate of cobaltous hydrate ($Co(OH)_2$) is produced.* A *very* strong solution of caustic alkali dissolves these precipitates, forming a blue solution.

Ammonia (AmOH) gives a slight blue precipitate which dissolves at once in excess, forming a reddish brown solution. Ammonium chloride prevents the precipitation.*

Sodium carbonate (Na_2CO_3) gives a rose-red precipitate that speedily changes to a rich blue colour.* These compounds are basic carbonates.

Ammonium carbonate (Am_2CO_3) gives a similar result, but the precipitate dissolves in excess of the reagent to form a fine purple solution.*

For other reactions see the next section.

COMPARATIVE REMARKS ON THE BASIC (OR METALLIC) RADICALS OF GROUP III.b

(ZINC, MANGANESE, NICKEL, AND COBALT)

Colour as affected by Temperature.—Zinc oxide is white, but it turns yellow when heated, changing back to white as it cools. This effect of increasing the temperature is according to the general rule. There is a tendency for white substances to become yellow at a high temperature, yellow to become red, red to become brown, and brown to become black, when the heating does not effect a change of composition. Shortly and generally it may be said that the tendency of substances is to be darker in colour when hot. This will be observed in many cases subsequently mentioned, but special notice may be taken of ferric oxide, which is red when cold and brown when hot, and of borax beads in general.

Oxidation in Alkaline Media, Reduction by Acids.—It will have been noticed in the case of manganese and cobalt compounds that oxidation takes place in the presence of alkalies, but not in the presence of acids. In fact, all highly oxidised manganese and cobalt compounds, such as manganates, permanganates, manganese peroxide, and cobalt peroxide, if heated with hydrochloric or sulphuric acid, are reduced to manganous or cobaltous salts as the case may be, the oxygen being either given off or taken up by something susceptible of oxidation. It is a general fact that metallic compounds are more readily oxidised in the presence of alkalies, and more readily reduced to a lower condition of oxidation in the presence of acids. This will be noticed particularly also in the case of iron and chromium compounds. Ferrous salts in solution with acids

will become slowly oxidised by the action of the air to ferric, but ferrous hydrate when precipitated with caustic soda or ammonia becomes oxidised so rapidly that many persons have never seen the pure unoxidised compound. Manganates and also chromates are produced in the presence of alkaline fluxes.   On the other hand, this general rule is not without exceptions, for a permanganate may be formed by the action of nitric acid and lead dioxide on a manganous salt.

Zinc forms only one oxide and series of salts by ordinary reactions.   A black nickelic hydrate ($Ni_2(OH)_6$) may be produced by passing chlorine into a solution of caustic soda containing nickelous hydrate in suspension, though the nickelous hydrate is unaffected by simple exposure to the air.   The black cobaltic hydrate ($Co_2(OH)_6$) may be produced by an analogous method to that which yields nickelic hydrate, but cobaltous hydrate is also oxidised by simple exposure to the air. There are other easily produced cobaltic compounds, such as potassium cobalticyanide ($K_6Co_2Cy_{12}$), and the double cobaltic potassium nitrite ($6KNO_2,Co_2(NO_2)_6,3H_2O$).   Manganous compounds by the action of chlorine or bromine in alkaline solutions yields the hydrated dioxide, and by further oxidation give the manganates and permanganates.   With regard to ease and extent of oxidation, therefore, these metals follow in the order (1) zinc, (2) nickel, (3) cobalt, (4) manganese.

The action of ammonia in the presence and absence of ammonium chloride is similar in the cases of manganese and magnesium salts, except that the result with manganese salts is complicated by the oxidisability of the compound to insoluble manganic hydrates.   The action doubtless is analogous also with zinc, nickel and cobalt salts, but as the hydrates of these metals dissolve in excess of

ammonia, it is impossible by adding more ammonia to
reprecipitate the hydrates.

Separation.—These four metals are separated from
those of groups four and five by the precipitation of their
sulphides with ammonium sulphide or with sulphuretted
hydrogen passed into an alkaline solution.

Zinc differs from the other three metals in that its
hydrate is soluble in sodium hydrate. The superior
volatility of metallic zinc is not of much practical use in
qualitative analysis.

Manganese differs from the other three in forming a
sulphide soluble in acetic acid.

Manganese and zinc form sulphides easily soluble in
dilute hydrochloric acid, while the sulphides of nickel and
cobalt are practically insoluble in it. Zinc and manga-
nese are often separated from nickel and cobalt by means
of this reaction; but the method is not to be preferred,
because the nickel and cobalt sulphides by exposure to
air so readily begin to oxidise to sulphates, which of
course dissolve in the dilute acid, that the separation is
only approximate. This is especially the case when nickel
and cobalt sulphides only are present, so that the proof of
the absence of zinc and manganese is likely to be unsatis-
factory. In the presence of either zinc or manganese, the
sulphuretted hydrogen given off by the action of the acid
on their sulphides tends to prevent the oxidation of the
nickel and cobalt sulphides, and fairly satisfactory results
may then be obtained.

Separation of Nickel and Cobalt.—The compounds of
these two metals are closely allied to one another in some
of their reactions. The methods by which they are
separated depend invariably upon the superior oxidisability
of certain cobalt compounds. By gradually adding a
solution of bleaching powder to an aqueous solution of a

mixture of cobalt and nickel salts, black cobaltic hydrate
is first precipitated, and this is followed by the black
nickelic hydrate as more of the bleaching powder is intro-
duced. This method of separation is not so useful in
dealing with small quantities as when working on a larger
scale.

Potassium cyanide (KCy) when added to the solution of
either a nickel or a cobalt salt gives a light-coloured pre-
cipitate of the cyanide $(M''Cy_2)$, which is readily dissolved
by adding more potassium cyanide, forming a double
cyanide $(2KCy,NiCy_2,$ and $4KCy,CoCy_2)$. Dilute hydro-
chloric acid reprecipitates the nickel or cobalt cyanide
from both solutions by decomposing the potassium cyanide.
But if the solutions of the double cyanides are boiled,
especially if there is a little free hydrocyanic acid present
(and this will be present if the solution to which the po-
tassium cyanide was added contained any free hydrochloric
acid), then the nickel compound remains unchanged, but
the cobalt compound is oxidised into potassium cobalti-
cyanide $(K_6Co_2Cy_{12})$, a stable salt that is not decomposed
by dilute hydrochloric acid. The oxidation of the cobalt
cyanide is attended with evolution of hydrogen if air is
excluded :—

$$2(4KCy, CoCy_2) + 2HCy = K_6Co_2Cy_{12} + 2KCy + H_2 ;$$
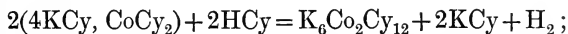
but in the presence of air, its oxygen effects the change,
and hydrogen appears not to be evolved :—

$$2(4KCy, CoCy_2) + 2HCy + O = K_6Co_2Cy_{12} + 2KCy + H_2O.$$
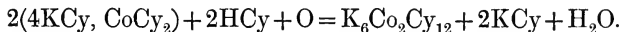
Hydrochloric acid is not a good precipitant for the nickel
salt in this separation, as it brings down some or it may
be all of the cobalt in addition as nickel cobalticyanide.
Sodium hypochlorite is preferable because it does not
suffer from this disadvantage, and also because of its

tendency to oxidise any remaining cobaltous cyanide that has not already been converted into the stable cobalti-cyanide. The hypochlorite must be added in considerable quantity, and the solution slightly warmed. The black nickelic hydrate is then precipitated, and the cobalt remains in solution. The action of the hypochlorite is represented thus :—

$$2NiCy_2 + NaClO + 5H_2O = Ni_2(OH)_6 + NaCl + 4HCy.$$
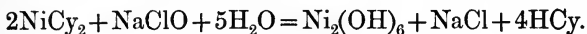
This method is generally to be recommended. If the hypochlorite does not readily precipitate the nickelic hydrate, a few drops of the solution may be taken separately and more hypochlorite added with gentle warming. If this gives a precipitate, more of the reagent must be added to the whole solution. The nickel and cobalt may both be confirmed by the borax beads they give, the cobalt after evaporating to dryness a few drops of the solution containing it.*

Potassium nitrite (KNO_2) if added to a solution containing nickel and cobalt salts gives a precipitate, because of the presence of hydrate and carbonate in the reagent. If then acetic acid is added to redissolve this precipitate, and sufficient also to give a strongly acid reaction to the solution, and it is allowed to stand, the nickel salt is not affected; but the cobalt compound is oxidised by the liberated nitrous acid, and there gradually separates potassium cobaltic nitrite ($6KNO_2, Co_2(NO_2)_6, 3H_2O$) as a yellow crystalline precipitate. By adding sodium carbonate or ammonium sulphide to the filtrate, the nickel will be precipitated as carbonate or sulphide as the case may be.

If ammonium chloride and a large excess of ammonia are added to a solution of a cobaltous salt, potassium ferricyanide gives a deep red colour when added to the

solution.   If a very little cobalt is present the solution is
tinted rose red, but a correspondingly small quantity of
ferricyanide must be added, or its yellow colour will
interfere with the distinctness of the tint.   No precipitate
is produced even on boiling, unless the solution is
abnormally strong or deficient in ammonia.   A solution
of a nickelous salt treated in the same way gives a
yellowish solution, and, on boiling, a precipitate of a
reddish-yellow to a yellowish-white colour.*   Under some
conditions the nickel precipitate is obtained with difficulty
or not at all; this test is therefore chiefly serviceable for
the detection of cobalt, and a little cobalt, even in the
presence of much nickel, is easily found by means of it.
Manganese salts, if present, give a white precipitate,
which is changed to brown by the addition of more
ferricyanide.

# THE BASIC (OR METALLIC) RADICALS OF GROUP III., SECTION A

Iron

Use ferrous sulphate ($FeSO_4,7H_2O$) and ferric chloride ($Fe_2Cl_6,12H_2O$ or $FeCl_3,6H_2O$).

When heated with fusion mixture on charcoal, iron compounds give a grey, metallic, magnetic powder, which can be separated as described under Nickel.

When iron compounds are heated in a borax bead, the bead becomes yellow in the outer flame and a bottle-green colour (the colour of common glass bottles) in the inner flame. Both colours are darker when the bead is hot, the first having a redder tint and the other more of an olive green.* Increasing the amount of iron also darkens the colours of the beads. Microcosmic salt gives similar colours, but the changes are not so marked.

Iron compounds are of two kinds, ferrous and ferric. The two chlorides are ferrous, $FeCl_2$, and ferric, $FeCl_3$ (or Fe_2Cl_6). The change from one into the other is effected by adding or removing chlorine, as the case may be.

Gaseous chlorine conducted into a solution of ferrous chloride combines with it to form ferric chloride. Nitric acid is a convenient oxidiser for converting ferrous salts into ferric, but hydrochloric or sulphuric acid should be present also :—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$
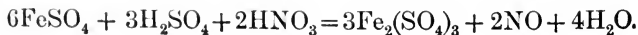
If a very small quantity of the iron salt is present, then bromine water is preferable. Permanganates and chromates also easily oxidise ferrous into ferric salts in the presence of acids.

Ferric salts may be reduced to ferrous by metallic zinc, sulphuretted hydrogen, sulphurous acid, stannous chloride and other analogous substances.

The reactions of ferrous compounds approximate to those of the other dyad metals of this group, namely, zinc, manganese, nickel and cobalt, while ferric compounds resemble in their behaviour the compounds of the other triad (or pseudo-tetrad) metals, namely, chromium and aluminium. It will be well to perform each reaction upon the ferrous and the ferric salt simultaneously, and to compare the results. It is however very difficult to get a solution of a ferrous salt quite free from ferric, because of the oxidising action of the air. The more sensitive reactions for ferric salts will probably give results with both solutions, but much more strongly with the ferric salt than with the small amount of ferric present in the ferrous salt.

Ammonia (NH_4OH) gives with solutions of ferrous salts a white precipitate of ferrous hydrate ($Fe(OH)_2$), which, by absorbing oxygen, so quickly changes to a dirty green that the colour of the unoxidised hydrate is rarely seen. On standing, those parts that are in the more immediate presence of the air change to brownish-red ferric hydrate ($Fe_2(OH)_6$).* Ammonium chloride prevents the precipitation from ferrous salts that are free from ferric, and ferric hydrate separates as oxygen from the air is taken up.

With ferric salts ammonia precipitates at once the brownish-red ferric hydrate ($Fe_2(OH)_6$),* the separation of which is in no way hindered by the presence of ammonium chloride.

Sodium hydrate (NaOH) behaves like ammonia, and the precipitates are not soluble in excess.

Ammonium sulphide (Am_2S) with ferrous salts gives a black precipitate of ferrous sulphide (FeS)* which is easily soluble in dilute hydrochloric, nitric or sulphuric acid. Ferrous sulphide is the only black sulphide readily soluble in dilute acids. If a very little iron is present the ferrous sulphide formed only imparts a greenish tint to the liquid.

With ferric salts a black precipitate is also produced, and it consists of ferrous sulphide mixed with sulphur.* The ferric sulphide decomposes as soon as produced, and there remain only the products of its decomposition :—

$$Fe_2Cl_6 + 3Am_2S = 2FeS + S + 6AmCl.$$
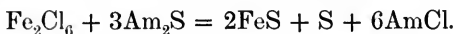
Sulphuretted hydrogen has very little effect upon solutions of ferrous salts, and none at all if the solution is acidified before passing the gas through it.

Ferric salts are reduced to ferrous with precipitation of sulphur,* thus :—

$$Fe_2Cl_6 + SH_2 = 2FeCl_2 + S + 2HCl.$$
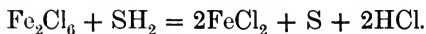
The yellow colour of the ferric salt gradually disappears as reduction takes place.

Sodium carbonate (Na_2CO_3) gives with ferrous salts a white precipitate of ferrous carbonate ($FeCO_3$) which darkens as it oxidises by exposure to the air.*

With ferric salts the hydrate is precipitated,* ferric carbonate not being known to exist :—

$$Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = Fe_2(OH)_6 + 6NaCl + 3CO_2.$$
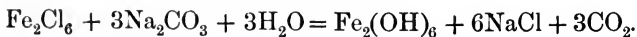
Barium carbonate ($BaCO_3$), which for the sake of convenience is added mixed with water as a milky liquid, has no action upon ferrous salts.

Ferric salts are completely precipitated by it as ferric hydrate ($Fe_2(OH)_6$) and a basic salt. To ensure a complete reaction the reagent should be added in sufficient quantity to impart a light colour to the iron precipitate because of the presence in the precipitate of the excess of barium carbonate.

Sodium acetate ($NaC_2H_3O_2$) produces no obvious change with ferrous salts.*

With ferric salts a deep red colour is produced, due to the formation of ferric acetate. The presence of a free acid such as hydrochloric or sulphuric, prevents the production of this colour until an excess of acetate is added. The addition of acids destroys the colour. If the solution is warmed a bulky, brownish-red precipitate of a basic acetate separates out.* Iron in the ferric condition may be completely precipitated by this reaction, but the precipitate should be filtered off while the solution is hot, as it partially dissolves on cooling.

Potassium ferrocyanide (K_4FeCy_6) gives with ferrous salts a nearly white precipitate of potassium ferrous ferrocyanide ($K_2FeFeCy_6$) which rapidly becomes blue by oxidation, even by mere exposure to the air.* The final product of oxidation is a dark blue compound (or mixture of compounds) analogous to Prussian blue or Turnbull's blue.

Ferric salts give a very dark blue precipitate of ferric ferrocyanide ($Fe_4Fe_3Cy_{18}$), called " Prussian blue." *

Potassium ferricyanide ($K_6Fe_2Cy_{12}$) gives with ferrous salts a very dark blue precipitate of ferrous ferricyanide ($Fe_3Fe_2Cy_{12}$), called " Turnbull's blue."* It is not distinguishable in colour from Prussian blue.

Ferric salts give no precipitate, but the colour of the mixed solutions is a reddish brown.* To ensure the absence of ferrocyanide and the consequent production of a blue precipitate, a crystal of the solid ferricyanide

should be washed, then shaken with water, and the solution obtained used at once.

The production of the above cyanides of iron is not interfered with by the presence of dilute acids. Caustic soda at once decomposes both Prussian blue and Turnbull's blue, with formation of ferric hydrate as residue and the alkaline ferrocyanide in solution. Turnbull's blue presumably at first gives ferrous hydrate and ferricyanide; but the ferricyanide immediately oxidises the ferrous hydrate as would be expected, for few oxidisable substances can withstand the action of an alkaline solution of a ferricyanide. It should be noticed that in both dark blue precipitates iron is present in the ferrous as well as the ferric condition. If the iron in both the solution being tested and the reagent is ferrous, a nearly white precipitate results; if they are both ferric, there is no precipitate.

Ammonium thiocyanate (AmCNS) gives no perceptible change with ferrous salts.* If a red colour is produced it is evidence that the ferrous salt is partly oxidised.

Ferric salts give a fine deep red colour, due to ferric thiocyanate $(Fe_2(CNS)_6)$.* This reaction is even more delicate than the production of Prussian blue. Hydrochloric acid does not interfere with it, but mercuric chloride destroys the colour. The red solution of ferric acetate is bleached by hydrochloric acid, but not by mercuric chloride, and is precipitated on heating; in these reactions it differs from the thiocyanate.

Hydrogen disodium phosphate (HNa_2PO_4) gives important reactions with iron salts; but it will be more convenient to consider these in connection with the section on phosphates than in this place.

Chromium

Use chromium chloride (Cr_2Cl_6,xH_2O or $CrCl_3,xH_2O$) or chrome alum ($K_2Cr_2(SO_4)_4,24H_2O$ or $KCr(SO_4)_2, 12H_2O$), and potassium chromate (K_2CrO_4) or dichromate ($K_2Cr_2O_7$).

In the borax bead chromium compounds give a fine green colour in either the inner or the outer flame.* Microcosmic salt gives similar results.

When fused with fusion mixture and nitre, preferable on a platinum support, a yellow mass is obtained, the colour being due to the production of alkaline chromate.* Other oxidisers, such as potassium chlorate and sodium peroxide, are efficient, or if the fusion mixture alone is used, the air will act as the oxidiser. In the last case of course the change will be more slow.

The principal chromium compounds are of two kinds, namely, salts of chromium and chromates. In the first the metal acts the part of the base, and in the second it is a constituent of the acid radical of the salts. An increased oxidation tends to produce or intensify acid properties; this was well shown in the case of manganese, and chromium is an example of the application of the same rule. The salt-forming oxide, chromic oxide, has the formula Cr_2O_3, and the acid oxide or anhydride is CrO_3, so that the proportion of oxygen to metal is exactly doubled in passing from the oxide to the anhydride. Chromic salts are green, or, less often, violet, while chromates are yellow or red; the change from one to the other can therefore be easily recognised.

The oxidation of chromic compounds to chromates is invariably effected in an alkaline medium. The fusion with an alkaline flux and an oxidiser has already been

described. When caustic soda is added to an aqueous solution of a chromium salt, a precipitate of chromic hydrate is produced, and excess of soda dissolves it. If to this solution a suitable oxidising agent is added, that is, one that will work in an alkaline solution, such as dioxide of lead, sodium hypochlorite, or sodium peroxide, and the mixture is warmed, the colour of the solution will change to yellow, demonstrating that a chromate has been produced. Sodium peroxide is efficient without the previous treatment with caustic soda. If lead dioxide is used, on acidification (preferably with acetic acid) the yellow lead chromate will be precipitated.* Equations should be written for these changes, bearing in mind that sodium hydrate is present, and that the proportion of oxygen that has to be added is equal to three atoms of oxygen to each two atoms of chromium present. The quantity of the oxidiser necessary in each case must be such that it will furnish this proportion of oxygen.

The reduction of chromates to chromic compounds is exactly the reverse of the change just considered. For each two atoms of chromium in the chromate three atoms of oxygen have to be removed. This is the key to the discovery of the amount of the reducing agent necessary. If potassium dichromate is warmed with strong sulphuric acid, this proportion of oxygen is evolved in the free state, thus :—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$
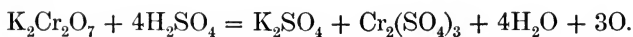
If strong hydrochloric acid is used, this oxygen combines with hydrogen of the acid, and chlorine is liberated instead, thus :—

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$
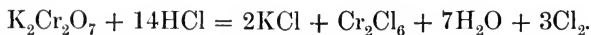
Sulphuretted hydrogen, sulphurous acid, oxalic acid, and

many other substances, in acid solutions, reduce chromates,* themselves of course being oxidised and yielding sulphur, sulphuric acid, and carbonic anhydride respectively from the three substances named.   Stannous chloride, ferrous salts and similar compounds, alcohol and other organic compounds, especially on heating, also reduce chromates.

As has been previously pointed out, such reductions as these are generally best effected in acid solutions, and the rule holds good in all the examples just given.   But sulphuretted hydrogen will effect the reduction of chromates also in an alkaline solution.   If excess of ammonium sulphide is added to a solution of potassium dichromate and the mixture is heated, sulphur is precipitated with green chromic hydrate,* thus :—

$$K_2Cr_2O_7 + 3Am_2S + 7H_2O$$
$$= 2KOH + Cr_2(OH)_6 + 6AmOH + 3S.$$
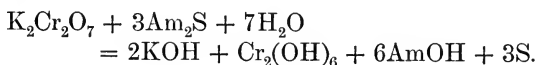
Here it may be observed that the three sulphur atoms liberated are exactly the equivalent of the three oxygen and the six chlorine atoms set free, as shown in the two previous equations.

The reactions given above are often of use in detecting chromium, particularly because of the colour changes that they produce.   Other reactions, produced by double decomposition, are given below for chromic salts and for chromates ; but they are not compared with each other, as was done with ferrous and ferric salts, because they are so different in their characteristics.

Chromic Salts

Ammonia (AmOH) gives with solutions of chromic salts a green precipitate of chromic hydrate ($Cr_2(OH)_6$).* Excess of the reagent often dissolves a little of the precipi-

tate, and a pink solution results.   Complete precipitation ensues on heating.

Sodium hydrate (NaOH) gives the same precipitate, and it dissolves readily in excess of soda to a green solution.   On heating the solution the chromic hydrate at once begins to separate out ; * but the heating must be continued for some time to ensure its complete precipitation.   Ammonium chloride precipitates chromic hydrate from its solution in sodium hydrate because it reacts with the soda to form sodium chloride and ammonia, neither of which can hold the chromic hydrate in solution.   In the presence of zinc salts, caustic soda gives a precipitate of a compound of zinc and chromium hydrates which does not dissolve in excess of the alkali.

Ammonium sulphide (Am_2S) gives the same precipitate,* chromic sulphide (like ferric sulphide) not being producible in aqueous solutions.   Ammonium sulphide is obtained by passing sulphuretted hydrogen into ammonia, and may therefore sometimes be regarded as these two substances in one.   In this case the sulphuretted hydrogen is inert and is therefore simply liberated, and the ammonia reacts as if it were alone.

Sodium carbonate (Na_2CO_3) gives a green precipitate,* which appears to be a basic salt.

Barium carbonate ($BaCO_3$) gives a green precipitate of a basic salt.   The precipitation is slow, and complete only after long standing.

Hydrogen disodium phosphate (HNa_2PO_4) gives a green precipitate of chromic phosphate ($Cr_2P_2O_8$),* soluble, like phosphates in general, in dilute hydrochloric acid, but also somewhat soluble in acetic acid, in this differing from the corresponding phosphates of iron and aluminium, and inclining to the general behaviour of the phosphates of the dyad metals.

Chromous salts, the analogues of ferrous salts, are known; but they are so much more readily oxidised than ferrous salts, and they so rarely occur, that it is not desirable to study them here.

Chromates

Alkaline chromates are yellow, and the dichromates are red. These chromates are converted into dichromates·by the addition of acids to their solutions, and the addition of alkalies changes the dichromates into chromates. These reactions can be clearly seen by the alteration of colour —yellow to red, or red to yellow.

For the following reactions use a solution of potassium chromate (K_2CrO_4).

Lead acetate ($Pb(C_2H_3O_2)_2$) gives a fine opaque yellow precipitate of lead chromate ($PbCrO_4$), which is completely soluble in caustic soda,* tardily soluble in dilute nitric acid, insoluble in acetic acid. Acetic acid is the best acid to have present in applying this reaction. By treating the yellow chromate with alkalies, not in excess, a fine vermilion-red basic chromate is obtained, to which the formula $PbCrO_4,PbO$ has been assigned. The alkali removes a part (to get a substance of the formula given exactly one-half) of the chromic anhydride.

Barium chloride ($BaCl_2$) gives a light yellow precipitate of barium chromate ($BaCrO_4$), soluble in hydrochloric acid, and not soluble in acetic acid.* For the reactions of chromates with strontium and calcium salts, see the sections dealing with the reactions of these metals.

Silver nitrate ($AgNO_3$) gives, from neutral or nearly neutral solutions only, a dark purplish red precipitate of silver chromate (Ag_2CrO_4), which dissolves readily in either dilute nitric acid or ammonia.* Potassium dichromate (or the normal chromate, with a little acid added

to form the dichromate) yields, with silver nitrate, silver dichromate ($Ag_2Cr_2O_7$), which is similar in appearance and behaviour to the normal chromate.

Mercurous nitrate ($Hg_2(NO_3)_2$) gives a dark red precipitate of basic mercurous chromate (Hg_2CrO_4,Hg_2O).* This is chiefly of interest because on ignition it leaves only green chromic oxide (Cr_2O_3).

Aluminium

Use aluminium chloride ($Al_2Cl_6,12H_2O$ or $AlCl_3,6H_2O$) or common alum ($Am_2Al_2(SO_4)_4,24H_2O$, or $AmAl(SO_4)_2,12H_2O$).

Heated on charcoal, aluminium salts with volatile acids leave a white infusible residue of alumina (Al_2O_3), and this, if moistened with a solution of cobalt nitrate and again heated, is coloured blue.* This reaction is of very little use, because the presence of other coloured substances interferes with it, and the nitrate of cobalt imparts a blue colour to many compounds under similar conditions. The distinction lies in the infusibility of the alumina, other substances that are coloured blue (borates, phosphates, silicates) being generally fusible.

Ammonia (AmOH) gives with solutions of aluminium salts a bulky white gelatinous precipitate of aluminium hydrate ($Al_2(OH)_6$),* which is slightly soluble in excess of ammonia, completely precipitated on boiling, and less soluble in the presence of ammonium chloride.

Sodium hydrate (NaOH) gives the same precipitate, and dissolves it readily on adding excess. The alumina is reprecipitated from this solution on adding ammonium chloride to it, or better, on first acidifying it with hydrochloric acid and then adding ammonia.* The latter method is preferable, because it avoids the unnecessary

excess of ammonia that is otherwise liberated by the caustic soda.

Ammonium sulphide (Am_2S) also precipitates the hydrate,* as aluminium sulphide cannot be produced in solution. The reaction is exactly analogous to the corresponding reaction with chromic salts.

Sodium carbonate (Na_2CO_3) gives a white precipitate of a basic carbonate of uncertain composition.*

Barium carbonate ($BaCO_3$) precipitates alumina slowly but completely, as hydrate mixed with basic salt.

Hydrogen disodium phosphate (HNa_2PO_4) gives a white gelatinous precipitate of aluminium phosphate ($Al_2P_2O_8$),* which, so far as its solubility in caustic soda and reprecipitation therefrom by ammonium chloride or hydrochloric acid followed by ammonia, cannot be distinguished from the hydrate. It is, however, insoluble in acetic acid, while the hydrate is soluble, or very nearly soluble, in excess of acetic acid, especially on heating.

Ammonium acetate ($AmC_2H_3O_2$) on heating precipitates a basic acetate of alumina.* The presence of a notable quantity of acetic acid prevents the precipitation, or, if added to the liquid containing the precipitate, dissolves it slowly in the cold, more rapidly on heating, though generally a small quantity remains undissolved.

COMPARATIVE REMARKS ON THE BASIC (OR METALLIC) RADICALS OF GROUP III.a

(IRON, CHROMIUM, AND ALUMINIUM)

Ferrous and ferric salts have already been compared. For the detection of iron and chromium in the presence of the other metals of Group III., ferrous compounds are generally oxidised into ferric, and chromates reduced to chromic compounds. Chromic salts invariably

give coloured solutions, so that in analytical work their presence can generally be traced from the first. Ferric salts with hydrochloric acid give yellow solutions. In the absence of chromium this is noticeable if the solution is not too dilute. Aluminium salts are white, and give colourless solutions.

The hydrates of the three metals can be precipitated by ammonium chloride and ammonia, and so they can be separated from zinc, manganese, nickel, and cobalt; and, on the whole, this is the best method for general qualitative purposes. The separation, however, is never complete, and may be very incomplete, unless done with care. As already shown, the ammoniacal solution containing manganese is oxidised by exposure to the air, and a dark-coloured manganic hydrate is precipitated. To prevent this oxidation, the solution should be boiled for a little to drive out dissolved air, ammonia added while at the boiling temperature, and the filtration done as soon as the ammonia has thoroughly mixed with the solution. As excess of ammonia tends to precipitate manganous hydrate, and ammonium chloride tends to prevent the precipitation, plenty of ammonium chloride should be added, and only a slight excess of ammonia. The ammonium chloride must be trusted to to prevent the precipitation of the hydrates of the zinc, nickel, and cobalt, and not an excess of ammonia. After every care has been taken, the separation will still be incomplete; but for ordinary purposes it is sufficient, unless some of the dyad metals are present in specially small quantities. The separation may be improved by redissolving the precipitate, and precipitating again with ammonium chloride and ammonia, when some of the hydrates of the dyad metals that were carried down the first time will now be left in the solution.

Barium carbonate is an excellent reagent for separating

iron, chromium, and aluminium from zinc, manganese, nickel, and cobalt; but the reaction is tedious, as the reagent must be allowed to act till the day following its addition in order to get the chromium and aluminium salts completely precipitated. After the separation, barium has to be got rid of from both the precipitate and the solution. For these reasons this method is not much used in qualitative work.

The solubility of alumina in caustic soda or potash is the reaction invariably employed for separating aluminium from iron in work of the character under discussion. This may be done either in aqueous solution or by fusion. In the latter case chromium salts are oxidised and form alkaline chromates, which also are soluble. It is convenient to use potassium nitrate for this purpose, because it is generally purer than any caustic alkali. By its decomposition when heated it gives some caustic potash which dissolves the alumina. After fusion of the three oxides with nitre, water will dissolve the chromate and the aluminium compound, leaving the iron as ferric oxide. The ferric oxide and the chromate are easily recognised, and the alumina can be precipitated by ammonium chloride, or by acidification with hydrochloric acid, followed by the addition of ammonia.

It seems, however, on the whole, to be preferable to use a solution of caustic soda. By adding this in excess to the dissolved chlorides in the cold, the aluminium and chromium hydrates at first precipitated are redissolved; but on warming in order to make the separation from the iron complete, the chromium hydrate is precipitated. The solution must be well boiled to ensure the complete precipitation of the chromium hydrate. The aluminium in the solution is easily recognised. The iron and chromium are readily separated by fusion with fusion

mixture and nitre, the chromium oxide being oxidised to an alkaline chromate which is soluble in water, and the iron remaining as ferric oxide.

The separation of these and other metals when they exist as or in the presence of phosphates, is given in connection with the section on phosphates.

The student should at this stage identify the members of this group in some solutions, each of which contains salts of a few of the metals selected to illustrate the different methods of separation.   The table given at page 175 should be followed, and the notes of the work should be written in a similar style to the specimen given for notes of the separation of the metallic radicals of Groups IV. and V. (see page 29).

THE BASIC (OR METALLIC) RADICALS OF GROUP II., FIRST SECTION, INCLUDING GROUP I.

Silver

Use silver nitrate ($AgNO_3$).

Silver salts, if mixed with fusion mixture and heated on charcoal, are reduced and yield the metal, which appears in the form of brilliant white malleable beads.* The carbonate of silver that is formed by double decomposition is decomposed by heat into carbonic anhydride, oxygen, and silver; the reducing action of the charcoal or of the blowpipe flame does not therefore of necessity take part in this reaction.

Hydrochloric acid (HCl) gives with solutions of silver salts a white curdy precipitate of silver chloride (AgCl). The precipitate darkens to a violet colour on exposure to light, at the same time losing a little of its chlorine. It is readily soluble in ammonia, and reprecipitated on acidification with nitric acid unless the quantity is very small.* It dissolves also readily in potassium cyanide and sodium thiosulphate, less readily in sodium sulphite. It dissolves to a considerable extent on warming it with concentrated hydrochloric acid or a strong solution of an alkaline chloride, but is precipitated again on dilution. When dry it readily melts, if heated, to a dark-coloured liquid, which

solidifies on cooling to a tough mass. Heated in a porcelain crucible over the blowpipe, it fumes and volatilises.

Sulphuretted hydrogen (H_2S) gives a black precipitate of silver sulphide (Ag_2S).* The precipitate is insoluble in dilute acids or alkalies, and also in alkaline sulphides or cyanides. Hot nitric acid readily attacks it forming nitrate of silver, some sulphur being set free.

Ammonium sulphide (Am_2S) gives the same precipitate.

Sodium hydrate ($NaOH$) gives a light brown precipitate of silver oxide (Ag_2O) which is insoluble in excess, but soluble in ammonia.* When dry it is readily decomposed by heat into the metal and oxygen.

Ammonia ($AmOH$) gives the same precipitate readily soluble in excess.* Ammonium salts prevent the precipitation.

Silver is easily precipitated in the metallic condition from its solutions by other metals. The metal used takes the place of the silver, thus :—

$$2AgNO_3 + Zn = Zn(NO_3)_2 + 2Ag.$$
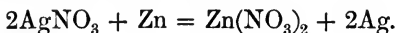
Copper may be used, then the white deposit of silver upon it is more clearly seen.* A small globule of mercury put into a drop of silver nitrate solution leads to the production of a crystalline mass of an amalgam of silver. Tin, lead, and iron also precipitate silver. Various organic substances, such as aldehyde, tartaric acid, formic acid, and glucose, reduce silver from its solutions, and from suitable solutions the precipitate appears as a bright coherent deposit on the surface of the glass in which the reaction takes place. In other cases the metal falls as a light grey precipitate ; but, by rubbing it with a hard surface, such as a knife-blade or glass rod, it may be burnished to its characteristic brilliant whiteness.

Mercury

Use mercuric chloride ($HgCl_2$) and mercurous nitrate ($Hg_2(NO_3)_2,4H_2O$, or $HgNO_3,2H_2O$).

Mercury is readily volatile on heating; and so are its salts, either with or without decomposition, except those of non-volatile acids, such as phosphoric and chromic acids, which leave a residue, free however from mercury. The oxides of mercury are decomposed by ignition into the metal and oxygen, so that salts, which in the case of other metals leave metallic oxides, in this case give metallic mercury and oxygen. Mercuric chloride, when heated, fuses and sublimes, mercurous chloride sublimes without fusion, mercuric sulphide volatilises slowly, giving a steel-coloured sublimate that becomes bright red when rubbed to powder. Mercuric sulphide, heated in the air, gives sulphurous anhydride by the combustion of its sulphur, and metallic mercury.
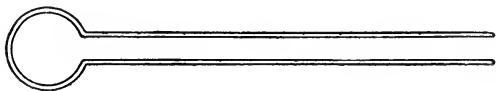
To exemplify the above statements, heat a little mercuric chloride in a bulb tube. Then repeat the experiment, but mix the mercuric chloride first with four or five times its bulk of dry sodium carbonate, and it is well to add a little more sodium carbonate to cover the mixture. In each case the bulb tube should be of about the size shown in the figure and held horizontally, no more of the substance being introduced than will lie in that part of the bulb that is below the level of the tube.*

F

In all such experiments the tube should be held in the fingers, because, if the open end gets too hot for the fingers, it is also probably too hot to condense the volatile matter that should be observed. The tube is held horizontally, indeed with the open end rather lower than the bulb, that any water condensing may not flow back to the hot bulb and break it.

Most mercury salts are reduced, giving a sublimate of metallic globules, when heated with sodium carbonate. The mercuric carbonate formed by the double decomposition is at once broken up by the heat into carbonic anhydride, mercury and oxygen, thus :—

$$HgCl_2 + Na_2CO_3 = 2NaCl + CO_2 + Hg + O.$$

Mercuric and mercurous compounds are very easily distinguished from each other, as will be obvious by the following reactions. Mercurous salts are converted into mercuric compounds by the ordinary oxidising agents, such as nitric acid, chlorine, and compounds that yield chlorine. Most mercurous salts show so much tendency to pass to the mercuric condition that one part of the salt will often oxidise another part, giving half the mercury as mercuric salt and half as metal. But mercurous salts are not oxidised to mercuric by exposure to the air. The general instability of mercurous compounds makes the production of them by reduction of mercuric compounds not a process of such ready application as in other similar cases.

Hydrochloric acid (HCl) gives no visible change when added to solutions of mercuric salts.

With mercurous salts it gives a dense heavy white precipitate of mercurous chloride (Hg_2Cl_2). The precipitate is readily oxidised and dissolved by chlorine or nitric acid. By boiling it with strong hydrochloric acid it is

soon changed into mercuric chloride and a globule of metallic mercury, thus :—

$$Hg_2Cl_2 = HgCl_2 + Hg.$$

Caustic soda and ammonia affect mercurous chloride in a similar way to mercuric chloride (see below) but the, mercurous products are both black. Sodium hydrate gives mercurous oxide (Hg_2O), but it is probably never free from some mercuric oxide and metal produced by its decomposition. Ammonia gives mercurous ammonium chloride (NH_2Hg_2Cl),* which however some regard as a mixture of mercuric ammonium chloride and mercury ($NH_2HgCl + Hg$).

Sulphuretted hydrogen (H_2S) gives with mercuric salts a black precipitate of mercuric sulphide (HgS).* If the reaction is done rather slowly, the precipitate at first is white and gradually becomes yellow, then brown, and finally black. This change of colour is characteristic of mercury salts, and may be observed, though not to so conspicuous an extent, in some other reactions mentioned below. Probably in every case the precipitate at first produced is a double compound of mercuric chloride with what will be the final product, in the case of the sulphuretted hydrogen a double salt of mercuric chloride and sulphide. When the reagent produces its full effect, all the chloride is changed into sulphide. Mercuric sulphide is not soluble in hydrochloric acid or moderately strong nitric acid, though nitric acid, on heating, eventually changes it into a white compound of sulphide and nitrate ($2HgS, Hg(NO_3)_2$). It is insoluble in sodium hydrate and in sodium hydrogen sulphide, but soluble in a mixture of the two ; from this solution it is reprecipitated by passing sulphuretted hydrogen. It is insoluble in ammonium sulphide. It is

readily attacked by aqua regia with formation of mercuric chloride.

Sulphuretted hydrogen, when passed into a solution of mercurous nitrate, gives a black precipitate of mercurous sulphide (Hg_2S),* though probably it always contains some metallic mercury and mercuric sulphide produced by its decomposition, and a further quantity of mercuric sulphide produced by the oxidising action of the liberated nitric acid. Nitric acid dissolves mercury out from the precipitate, leaving mercuric sulphide or the white product of the action of the nitric acid on the sulphide.

Ammonium sulphide (Am_2S) gives with mercury salts the same sulphides that sulphuretted hydrogen produces.

Sodium hydrate (NaOH) gives with mercuric salts a precipitate that is light coloured at first, but very quickly passes into a yellow, and darkens further to a reddish tint of yellow on heating. It is mercuric oxide (HgO).* It is somewhat soluble on adding excess of the precipitant, and ammonia added to the solution so obtained gives a white precipitate. The presence of alkaline salts prevents or retards the precipitation of the oxide; but if ammonium chloride is present a white precipitate is produced instead.

With mercurous salts caustic soda gives a black precipitate of mercurous oxide (Hg_2O),* mixed probably always with mercuric oxide and metallic mercury.

Ammonium hydrate (AmOH), when added to a solution of mercuric chloride, gives a white precipitate of mercuric ammonium chloride, (NH_2HgCl).* This is the substance known as "white precipitate" in pharmacy.

When added to mercurous nitrate, ammonia gives a black precipitate of a basic mercurous ammonium nitrate ($2(NH_2Hg_2NO_3)$, Hg_2O).* This may be merely a mixture

of the corresponding mercuric compound and mercury $(2(NH_2HgNO_3), HgO + 3Hg)$.

Sodium carbonate (Na_2CO_3) gives with mercuric salts a precipitate that is at first white, but soon changes through yellow to a brownish-red basic carbonate $(HgCO_3, 2HgO)$.* The precipitate dissolves in excess of the reagent, especially on warming, giving a solution in which ammonia produces a white precipitate. When the red basic carbonate is dissolved in sodium carbonate, a slight white turbidity is generally left. Alkaline salts, such as potassium chloride, retard or prevent the precipitation; but if ammonium chloride is present a copious white precipitate is obtained.

Potassium iodide (KI) gives with mercuric salts a bright red precipitate of mercuric iodide (HgI_2) which is soluble in excess of either the mercuric salt or the potassium iodide.*

Stannous chloride $(SnCl_2)$ reduces mercuric salts, giving first a white precipitate of mercurous chloride (Hg_2Cl_2), and, with excess of the reagent and warming, a grey precipitate of metallic mercury.* By boiling with hydrochloric acid the mercury easily unites into a globule.

With mercurous salts, stannous chloride first precipitates mercurous chloride by double decomposition, and then reduces it to the metal.

Many metals replace mercury in its solutions, whether of mercuric or mercurous salts, the mercury being deposited on the metal and forming in some cases an amalgam with it. A strip of clean copper, if put into a slightly acid solution that contains mercury, soon becomes coated with the metal, and a gentle rubbing will show the characteristic silvery-white surface of the deposit. By heating the coated metal the mercury is readily volatilised.*

Zinc and iron also precipitate mercury from its solutions, in every case the metal used taking the place originally occupied by the mercury :—

$$HgCl_2 + Zn = ZnCl_2 + Hg.$$
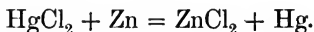
Lead

Use lead nitrate ($Pb(NO_3)_2$).

Heated on charcoal with fusion mixture, compounds of lead are quickly reduced to the metal, which forms an easily fusible bead, and a part of the metal, being volatilised, passes through the flame, colouring it blue, and, being oxidised when it comes into contact with the air, it deposits on the cooler surrounding part of the charcoal as a yellow incrustation. The incrustation of oxide is easily volatilised when touched with even the tip of the oxidising flame. The bead, when detached from the charcoal, should be flattened by striking it with a pestle on the bottom of an inverted mortar. It is very malleable, and if drawn across paper leaves a streak, the paper being hard enough to act as a file to the soft metal.*

Hydrochloric acid (HCl) gives from solutions of lead salts that are not too dilute a white crystalline precipitate of lead chloride ($PbCl_2$), which is easily soluble in hot water, and crystallises out on cooling.* At the best hydrochloric acid precipitates lead only incompletely.

Sulphuretted hydrogen (H_2S) gives a black precipitate of lead sulphide (PbS),* which is insoluble in dilute acids and unaffected by alkalies or alkaline sulphides. Hot nitric acid readily attacks it, forming chiefly lead nitrate, unless the acid is very strong, when lead sulphate will be the chief product. In the presence of much hydrochloric acid sulphuretted hydrogen may give no precipitate, or a

brownish red precipitate of a compound of sulphide and chloride of lead. In either case, on diluting sufficiently, the black sulphide separates.

Ammonium sulphide (Am_2S) gives the same precipitate.

Sodium hydrate (NaOH) gives a white precipitate of lead hydrate ($Pb(HO)_2$), probably mixed with more or less of a basic salt. The precipitate dissolves at once on adding excess of caustic soda.* With a smaller excess of the alkali the solution is promoted by warming.

Ammonium hydrate (AmOH) gives a similar precipitate, not soluble in excess,* but easily soluble on adding caustic soda to the liquid containing it.

Sodium carbonate (Na_2CO_3) gives a white precipitate of a basic carbonate, which probably approximates to the composition expressed by the formula $2PbCO_3$, $Pb(OH)_2$,* but is very variable according to the conditions under which it is produced. It is not soluble in excess.

Potassium chromate (K_2CrO_4) gives a dense yellow precipitate of lead chromate ($PbCrO_4$), which dissolves completely on the addition of caustic soda.* It is insoluble in acetic acid, dissolves in a considerable excess of dilute nitric acid, and is reprecipitated on the addition of an alkaline acetate.

Sulphuric acid (H_2SO_4) gives a white precipitate of lead sulphate ($PbSO_4$).* The precipitation is more complete in the presence of an excess of dilute sulphuric acid than in water, and still more complete on the addition of an equal bulk of alcohol. Lead sulphate is speedily converted into chloride and dissolved by heating it with strong hydrochloric acid, and on cooling the solution, lead chloride crystallises out. It dissolves completely in caustic soda, in sodium thiosulphate, and in a strong solution of ammonium acetate, and also in the ammonium salts of some other acids both inorganic and organic. From its

solution in ammonium acetate it is reprecipitated by sulphuric acid; but potassium chromate or ammonium sulphide are to be preferred as precipitants.

Potassium iodide (KI) gives a yellow precipitate of lead iodide (PbI_2),* soluble in excess of the reagent. It is similar to the chloride in being soluble in hot water, and crystallising out as it cools.

Metallic zinc or *iron* precipitates metallic lead from solutions of its salts as a grey spongy mass* or a crystalline growth. The familiar "lead tree" is obtained by suspending a piece of zinc in a solution of lead acetate. The zinc, of course, takes the place of the lead in the solution, forming zinc acetate.

The most common oxides of lead are litharge (PbO), red lead (Pb_3O_4 or Pb_4O_5), and the brown oxide (PbO_2). By ignition the higher oxides are reduced to the monoxide. The oxygen in excess of the monoxide is available for oxidation purposes, as in the case of manganese oxides.

Bismuth

Use bismuth oxide (Bi_2O_3) or basic nitrate for the reaction on charcoal, and bismuth nitrate ($Bi(NO_3)_3,5H_2O$), or the oxide dissolved in as little nitric acid as possible for the reactions in solutions, except where stated otherwise.

Bismuth salts are reduced and yield the metal when heated with fusion mixture on charcoal, giving a bead that is very brittle. A little potassium cyanide may with advantage be added to the fusion mixture to facilitate the reduction. When detached from the charcoal and flattened, it will perhaps appear to be malleable; but an attempt to pick it up on the point of a knife will show that in flattening it it has been reduced to powder. The

metal being easily volatile, an incrustation of oxide is formed on the cooler parts of the charcoal, that is yellow when cold, and orange-coloured when hot. It is volatile when touched with the blowpipe flame, and does not colour the flame.*

Sulphuretted hydrogen (H_2S) gives with solutions of bismuth salts a black precipitate of bismuth sulphide (Bi_2S_3),* which is not soluble in dilute acids, alkalies, or alkaline sulphides. It is readily attacked and dissolved by moderately strong nitric acid. Solutions that contain a large quantity of a free mineral acid should be diluted before passing sulphuretted hydrogen, or the reaction will be retarded.

Ammonium sulphide (Am_2S) gives the same precipitate.

Sodium hydrate (NaOH) gives a white precipitate of bismuth hydrate ($Bi(OH)_3$),* which is insoluble in a moderate excess of the reagent. When heated with a considerable excess of caustic soda it dissolves; but the precipitate appears again on cooling, especially if more water is added.

Ammonia (AmOH) gives the same precipitate.*

Sodium carbonate (Na_2CO_3) gives a white precipitate of a basic bismuth carbonate (($BiO)_2CO_3$).*

Potassium chromate (K_2CrO_4) gives a yellow precipitate of a basic bismuth dichromate (($BiO)_2Cr_2O_7$). The precipitate is easily dissolved by adding dilute nitric or hydrochloric acid to the solution from which it has been precipitated,* or even in acetic acid, if a sufficient excess is added, especially on warming. It is soluble in ammonium acetate. If dissolved in the least quantity of nitric acid, ammonium acetate first reprecipitates a part of it, and then redissolves it. Sodium acetate reprecipitates, but does not dissolve it again in excess. It is not soluble in a moderate quantity of caustic soda; but, if washed and heated with a considerable excess, it is dissolved. A red

more basic chromate sometimes separates when heating the precipitate with caustic soda. The properties of bismuth chromate should be compared with those of lead chromate.

Stannous chloride ($SnCl_2$), followed by *sodium hydrate* (NaOH), gives a black precipitate of bismuth suboxide (BiO) insoluble in excess of the reagent.* The stannous chloride alone would give with caustic soda a white precipitate readily soluble in excess. The stannous chloride reduces the bismuth salt, being itself converted into an alkaline stannate, thus :—

$$2Bi(OH)_3 + SnCl_2 + 4NaOH$$
$$= 2BiO + Na_2SnO_3 + 2NaCl + 5H_2O.$$
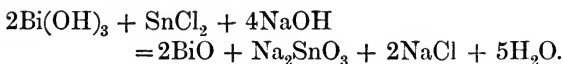
The bismuth hydrate in the equation is the product of the action of the sodium hydrate on the bismuth salt.

Glucose or grape sugar also reduces bismuth oxide in the presence of caustic soda on warming, with production of a black precipitate.

Potassium iodide (KI) gives a dark brown precipitate of bismuth iodide (BiI_3),* soluble in a large excess of the reagent, and reprecipitated by adding more water.

Water (H_2O) generally decomposes normal salts of bismuth, giving a precipitate of a basic salt and an acid or acid salt in solution. The action of water is most notable in the case of bismuth chloride ($BiCl_3$). Dissolve a small quantity of oxide of bismuth in as little strong hydrochloric acid as is sufficient, and add water a drop at a time. A permanent white precipitate will soon be produced. Add now hydrochloric acid (dilute will serve) very gradually until the precipitate has dissolved. More water will reproduce the precipitate more acid dissolve it, and so on. The precipitate is bismuth oxychloride (BiOCl).* In this case the acid tends to dissolve the precipitate and the

water to produce it, and whether the precipitate is produced or dissolved depends on the *proportion* of the oppositely acting reagents present. To make sure, therefore, of getting the precipitate from a solution of bismuth chloride that has not the minimum quantity of acid in it, plenty of water should be used, say, for qualitative purposes, even half a pint, and the solution added to it.

A higher oxide of bismuth is known (Bi_2O_5) and some compounds of it. These are called bismuthic compounds, and those treated of above, to distinguish them, are called bismuthous compounds. Bismuthic compounds are of so comparatively little importance and so rarely met with, that it is generally sufficient to use the word "bismuth," as is done above, instead of "bismuthous."

Bismuthic oxide is a bright red powder. It is produced by passing chlorine into a strong solution of caustic potash that contains bismuthous hydrate in suspension. It will be remembered that this is a common method of producing highly oxidised metallic compounds.

Copper

Use cupric sulphate ($CuSO_4,5H_2O$).

Heated on charcoal with fusion mixture to which a little potassium cyanide may be added, copper compounds are reduced and yield red metallic copper. An expert user of the blowpipe will be able to fuse the little globules together to form a larger one, but there is no need to do this.* The red colour that the separated metal imparts to the remaining mass is sufficient, or, if the residue is ground in a mortar and elutriated, spangles of small flattened globules of the bright red metal will remain. There is no incrustation, as neither copper nor its oxide is volatile at the temperature employed.

Heated on a borax bead, copper compounds give a blue bead which inclines to be green when hot.   In the reducing flame the compound is reduced to a red powder (the metal or suboxide probably), which may change the colour of the bead to an opaque red, or, if kept fused long enough, will settle to one side of the bead and leave the rest colourless.

Copper oxide and many other copper compounds, when heated on a platinum wire, colour the flame green.   If the wire is dipped into hydrochloric acid and then heated, the flame will be coloured a bright blue, the characteristic colour produced by cupric chloride.*

Sulphuretted hydrogen (H_2S) gives in solutions of cupric salts a brownish black precipitate of cupric sulphide (CuS)* which is insoluble in dilute acids and alkalies, and insoluble in alkaline sulphides except that ammonium sulphide dissolves it slightly, especially if yellow.   It is soluble in potassium cyanide, and readily attacked and dissolved by moderately strong nitric acid.   The sulphide is not precipitated in the presence of a very large excess of a free mineral acid.   Exposed to air when moist, it at once begins to oxidise on the surface to sulphate, so that the precipitate cannot be washed with plain water without loss by solution.

Ammonium sulphide (Am_2S) gives the same precipitate.

Sodium hydrate ($NaOH$) gives a light blue precipitate of cupric hydrate ($Cu(OH)_2$), which, on heating the liquid in which it has been formed, loses a part of its combined water and becomes black ($3CuO,H_2O$).*   Many organic substances, such as tartrates, citrates, sugar, etc., prevent the precipitation, and the alkali then produces a deep blue solution.

Ammonia ($AmOH$) gives at first a greenish blue precipitate of a basic salt; but this soon dissolves on

adding ammonia, and forms a very fine deep blue solution.*
The copper probably replaces some of the hydrogen of
the ammonium in the ammonium salt ($4NH_3,CuSO_4,H_2O$).
This tetra-ammonio-cupric sulphate may be expressed
$(NH_3)_2CuO, (NH_4)_2O, SO_3$, the first group differing from
the second in having two of its hydrogen atoms replaced
by copper.

Ammonium carbonate (Am_2CO_3) behaves in a similar
manner to ammonia.*

Sodium carbonate (Na_2CO_3) gives a greenish blue
precipitate of a basic cupric carbonate ($CuCO_3,Cu(OH)_2$),
which, on boiling the liquid it is suspended in, is
decomposed into the black hydrate ($3CuO,H_2O$).*

Potassium cyanide (KCy) gives a greenish precipitate
of cupric cyanide ($CuCy_2$) readily soluble in excess. The
solution of the double cyanide formed is not coloured by
alkalies nor precipitated by sulphuretted hydrogen.*
Potassium cyanide removes the colour from alkaline
solutions of cupric salts.

Potassium ferrocyanide (K_4FeCy_6) gives a reddish brown
precipitate of cupric ferrocyanide (Cu_2FeCy_6)* which is
not affected by dilute acids. In very weak solutions of
cupric salts only a reddish tint is produced. This is a
delicate reaction, but sulphuretted hydrogen will reveal a
smaller amount of copper than the ferrocyanide, though
the latter gives a more characteristic change.

Metallic zinc or *iron* precipitates metallic copper from
the solutions of its salts, the metals being coated with a
red deposit, but if the precipitate is of a spongy
consistency it will appear reddish brown. A better test is
to put the copper solution into a platinum crucible or
capsule, and drop in a small piece of zinc, the copper
then deposits on the platinum. Or a piece of platinum
foil (which should be quite clean) may be put in the

copper solution which is contained in a porcelain dish, and a piece of zinc dropped on to the foil.*

Cuprous salts do not often occur, but they are easily prepared. If a small quantity, say a gram, of cupric oxide is introduced into a test tube, about double its weight of metallic copper added, and then strong hydrochloric acid, and the mixture is agitated and boiled, the green colour of the cupric chloride will soon be replaced by the brown colour of a solution of cuprous chloride (which itself is colourless) mixed with a little cupric salt. If the solution is poured into water a white precipitate of cuprous chloride (Cu_2Cl_2) is deposited.* This precipitation by water must not be confused with the action of water on bismuth chloride which precipitates the oxychloride; here it is merely that cuprous chloride is soluble in strong hydrochloric acid but not in water. Diluting the acid therefore causes its deposition.

Cuprous oxide (Cu_2O) may be prepared from a cupric salt (cupric sulphate) by adding to its solution some glucose or grape sugar and then some caustic soda and heating the solution. A yellow cuprous hydrate ($Cu_2(OH)_2$) appears at first, but this soon changes to the bright red oxide.* By the action of caustic soda on cuprous chloride the hydrate is produced in the cold and the oxide on heating.

Potassium iodide (KI) if added to a solution of a cupric salt gives a white precipitate of cuprous iodide (Cu_2I_2), and iodine is liberated,* thus :—

$$2\ CuSO_4 + 4KI = Cu_2I_2 + I_2 + K_2SO_4.$$
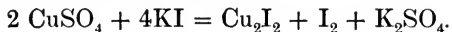
By adding a solution of ferrous sulphate or sulphurous acid the iodine is changed to hydriodic acid and the white cuprous iodide remains alone.

Ammonium thiocyanate (AmCNS) gives with cupric salts

a black precipitate of cupric thiocyanate ($Cu(CNS)_2$, but in the presence of sulphurous acid it gives a white precipitate of cuprous thiocyanate ($Cu_2(CNS)_2$).*

Cadmium

Use cadmium sulphate ($CdSO_4,4H_2O$) or cadmium chloride ($CdCl_2,2H_2O$).

Cadmium compounds when heated on charcoal with fusion mixture to which a little potassium cyanide may be added, are reduced and yield the metal; but as it is volatile at even a lower temperature than that employed for its reduction, it all passes away as vapour as soon as reduced, and gives only a reddish brown incrustation of cadmium oxide (CdO) as evidence of its presence.*

Sulphuretted hydrogen (H_2S) gives from solutions of cadmium salts a fine yellow precipitate of cadmium sulphide (CdS) * which is insoluble in alkalies, alkaline sulphides and potassium cyanide, and in very dilute acids. It is soluble in dilute sulphuric acid when heated with it, also in moderately dilute hydrochloric and nitric acids. No precipitate is produced in a too acid solution until it is diluted or partly neutralised.

Ammonium sulphide (Am_2S) gives the same precipitate.*

Sodium hydrate (NaOH) gives a white precipitate of cadmium hydrate ($Cd(OH)_2$),* not soluble in excess of the reagent.

Ammonia (AmOH) gives the same precipitate and readily dissolves it in excess.*

Sodium carbonate (Na_2CO_3) or *ammonium carbonate* (Am_2CO_3) gives a white precipitate of cadmium carbonate ($CdCO_3$),* not soluble in excess of either reagent, but easily soluble in ammonia or in cyanide of potassium.

Ammonium thiocyanate (AmCNS) gives no precipitate with cadmium salts, either with or without sulphurous acid.

COMPARATIVE REMARKS ON THE BASIC (OR METALLIC) RADICALS OF GROUP II., FIRST SECTION— INCLUDING GROUP I.

(SILVER, MERCURY, LEAD, BISMUTH, COPPER, AND CADMIUM)

The sulphides of all these metals are precipitated by sulphuretted hydrogen from acid solutions of their salts, and in this reaction this group differs from all the preceding groups that have been considered. The sulphides are not soluble in alkalies, and in this they differ from the sulphides of the members of the second section of this group.

Solutions of the salts of silver, lead, and mercury in the mercurous condition, give precipitates of the chlorides of these metals by the addition of hydrochloric acid. These three metals are classed together as Group I. because it is necessary in general work to acidify the solution, and hydrochloric acid is as a rule preferred for this purpose. It is easy to identify either of these three chlorides when they are precipitated together, for lead chloride is soluble in hot water, silver chloride is soluble in ammonia (though not completely in the presence of mercurous chloride), and mercurous chloride is blackened by ammonia.

Silver is chiefly characterised by the insolubility of its chloride, for lead chloride is soluble in hot water, and mercurous chloride is easily oxidised to the soluble mercuric chloride.

Mercury is distinguished from almost all other metals by its volatility, and from all others by the fact that the
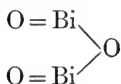
metal itself is a liquid at ordinary temperatures. Mercury and silver are the only metals considered in this volume whose oxides are decomposed by heat giving the metal itself. They are almost "noble metals," but their chlorides are not decomposed by heat alone. Mercury compounds are remarkable for the ease with which the metal may be obtained in the place of some of the hydrogen of ammonium compounds. The compounds of other metals, such as copper, cobalt, and chromium, show a similar tendency. Mercury and copper are alike also in forming lower chlorides as white compounds insoluble in water, and not so stable under ordinary conditions as the higher soluble chlorides. Mercuric sulphide is the most difficult to attack by acids of all the metallic sulphides, it resists even strong nitric acid. This property is utilised in its separation.
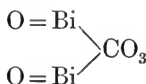
Lead is exceptional chiefly because of the insolubility of its sulphate. No other metal of Groups I., II., and III. forms an insoluble normal sulphate.

Bismuth is remarkable chiefly on account of the decomposition of its salts by water giving precipitates of basic salts, especially the chloride. Antimony chloride shows a similar reaction, and many other metallic chlorides do in a small degree, so that it is not the character of the reaction but the extent of it that is remarkable in the behaviour of bismuth compounds. The alternate precipitation and solution caused by adding hydrochloric acid and water in turn, is comparable with the alternate precipitation and solution caused with solutions containing magnesium or manganese, when ammonium chloride and ammonia are added alternately. The more of either that is present, the more of the other must be added to produce its own effect. Many bismuth salts are basic to the same extent, and are conveniently expressed by representing
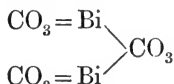
the monad group (BiO) as taking the place of each atom of hydrogen in the acid. This is seen in the carbonate, bichromate, and the oxychloride, among those salts mentioned above. These are good illustrations of the exact nature of basic salts :—

$$
\begin{array}{ccc}
\begin{array}{c} O=Bi \\ \diagdown \\ O=Bi \end{array}\!\!\!\!O &
\begin{array}{c} O=Bi \\ \diagdown \\ O=Bi \end{array}\!\!\!\!CO_3 &
\begin{array}{c} CO_3=Bi \\ \diagdown \\ CO_3=Bi \end{array}\!\!\!\!CO_3 \\
\text{The oxide} & \text{Basic} & \text{Normal} \\
\text{or base.} & \text{carbonate.} & \text{carbonate.}
\end{array}
$$

The normal carbonate probably does not exist.

Copper is a red metal, and generally forms blue or green compounds ; but some are white, some black, some red, and the ferrocyanide is chocolate brown. No other metal treated of in this volume forms a reddish brown ferrocyanide. In solution, copper salts are generally blue or green ; and as nickel salts in solution are generally green, it is useful to compare the reactions of copper and nickel together.

Cadmium is distinguished by its yellow sulphide which is insoluble in alkaline sulphides. The sulphides of other metals (tin, arsenic, and antimony) that are yellow are soluble in alkaline sulphides. Cadmium is closely allied to zinc. The sulphides of both metals are precipitated by sulphuretted hydrogen although a little free hydrochloric or sulphuric acid may be present, and in the presence of much free acid neither is precipitated. But it is possible to have an amount of acid that will prevent zinc sulphide from being formed and that will not prevent cadmium sulphide from precipitation, and that is why these metals are classified in separate groups. The tendency of cadmium sulphide to escape precipitation in Group II., the metal then passing into Group III., must be borne in mind.

Separation.—These metals are separated from Groups III., IV., and V. by precipitating their sulphides by means of sulphuretted hydrogen in a slightly acid solution. Mercury is generally separated from the others by taking advantage of the insolubility of its sulphide in nitric acid. As lead sulphide may be oxidised partly to sulphate, or as sulphuric acid may be formed by the oxidation of the sulphur in the sulphides that are attacked by the nitric acid, this sulphuric acid precipitating some of the lead, it is preferable to precipitate all the lead as sulphate along with the residual mercury sulphide, by adding sulphuric acid and alcohol. The lead sulphate can be separated from the mercury sulphide in many ways. It may be dissolved in ammonium acetate (or other similar salt solution), or in hydrochloric acid, which should be strong and hot, or in caustic soda, but this is not to be preferred because of its possible action on the mercury sulphide. It may be heated with a solution of sodium carbonate to transform it into carbonate, washed and then dissolved in dilute nitric or acetic acid.

The solution containing the copper, bismuth, and cadmium will be green if an appreciable quantity of copper is present. Ammonia precipitates the hydrates of these metals, but an excess dissolves those of copper and cadmium. The bismuth hydrate can easily be proved to be really due to bismuth, but as lead hydrate would be precipitated here unless the metal had been previously removed, it is better to avoid a test that might in any way incline towards the confusion of lead and bismuth hydrates. The use of the chromate as confirmation is, therefore, not to be recommended. The production of the black suboxide, by dissolving the precipitate in hydrochloric acid and adding stannous chloride and caustic soda, or the precipitation of the oxychloride, by

dissolving it in hydrochloric acid and pouring the solution into water, are reactions that cannot lead to the mistaking of a precipitate due to lead for bismuth hydrate.

The ammoniacal solution containing the copper and cadmium will be blue if even only a little copper is present. The two sulphides may be precipitated from this solution and then separated. As copper sulphide is slightly soluble in ammonium sulphide and cadmium sulphide is soluble in warm dilute mineral acids, it is best to acidify the solution with acetic acid before passing sulphuretted hydrogen. By boiling the mixed sulphides with dilute sulphuric acid, cadmium sulphide is dissolved, or by warming them with potassium cyanide solution the copper sulphide is dissolved, in each case the other remaining undissolved. But for mere identification, separation is not necessary. If a part of the ammoniacal solution is acidified with acetic acid and potassium ferrocyanide is added, the characteristic precipitate of copper ferrocyanide cannot fail to be seen. To test for cadmium, add to the remainder of the solution a little more potassium cyanide than is sufficient to cause the blue colour to disappear, and copper sulphide will then not be precipitated by sulphuretted hydrogen, while cadmium sulphide will come down at once. It is possible to separate copper and cadmium in solution by adding ammonium carbonate, excess of which dissolves the copper carbonate and not the cadmium carbonate, but the ammonium carbonate must be free from ammonia or the cadmium carbonate will be also dissolved. Or copper may be precipitated by ammonium thiocyanate in presence of sulphurous acid, cadmium remaining in solution.

THE REMAINING MEMBERS OF GROUP II.—
THE SECOND SECTION

Tin

Use stannous chloride ($SnCl_2, 2H_2O$).

When heated on charcoal with fusion mixture, or preferably a mixture of sodium carbonate and potassium cyanide, tin compounds give beads of the metal which may be easily run together. The bead is white and malleable, but not soft enough to mark paper like a bead of lead. The metal being volatile, a white incrustation of oxide forms around on the charcoal.*

A very small quantity of a stannous salt added to a borax bead that has been coloured blue by means of a copper salt, will on reheating the bead reduce the copper compound and form a red bead. The reduction can be effected without the tin salt by the reducing flame alone, but the tin salt causes an immediate change.

Sulphuretted hydrogen (H_2S) gives with solutions of stannous salts a dark brown precipitate of stannous sulphide (SnS) which is insoluble in dilute acids, soluble in strong hydrochloric acid, soluble in sodium hydrate and reprecipitated unchanged on acidification.* It is insoluble in ammonia and in colourless ammonium sulphide, but soluble in yellow ammonium sulphide with conversion into a stannic salt, and is precipitated on acidification as the yellow stannic sulphide (SnS_2). Nitric acid attacks the

sulphide with formation of the insoluble metastannic acid, a hydrated form of the dioxide (SnO_2).

The stannous sulphide when dissolved in alkalies behaves like an anhydride and produces alkaline salts. Now if an anhydride and alkali are both oxygen compounds, as in ordinary cases, the resulting salt is an oxy-salt, as, for example :—

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$
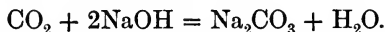
If the anhydride and the alkali are both sulphur compounds, a thio-salt results, thus :—

$$SnS + Am_2S_2 = Am_2SnS_3.$$
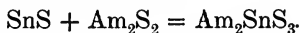
Here the yellow ammonium sulphide gives ammonium thiostannate. On acidification of this solution we have the following change :—

$$Am_2SnS_3 + 2HCl = SnS_2 + 2AmCl + H_2S.$$

If the anhydride is a sulphur compound and the alkali an oxygen compound, then both oxy- and thio-salts result, as in the following case :—

$$2SnS + 4NaOH = Na_2SnO_2 + Na_2SnS_2 + 2H_2O.$$
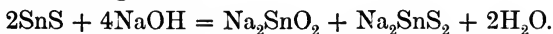
Sodium stannite and sodium thiostannite are probably produced. On acidification the stannous sulphide is reprecipitated, thus :—

$$Na_2SnO_2 + Na_2SnS_2 + 4HCl = 2SnS + 4NaCl + 2H_2O.$$

Ammonium sulphide (Am_2S) gives the same precipitate as sulphuretted hydrogen, soluble in excess if the reagent is yellow.

Sodium hydrate (NaOH) gives a bulky white precipitate of stannous hydrate ($Sn(OH)_2$) which readily dissolves in excess of the reagent.*

Ammonia (AmOH), *ammonium carbonate* (Am_2CO_3), and *sodium carbonate* (Na_2CO_3) each gives the same precipitate, and does not dissolve it on adding excess.*

Stannous chloride ($SnCl_2$) is converted into stannic chloride ($SnCl_4$) by many processes of oxidation. A convenient way of preparing a small quantity of stannic chloride for experimental purposes is to dissolve stannous chloride by warming it in rather more strong hydrochloric acid than is sufficient to cover it, and while still warm to add potassium chlorate crystals, a little at a time, and until the liquid and the gases evolved are yellow, indicating that chlorine is no longer being absorbed. The free chlorine is boiled off and water added.*

Nitric acid must not be used except with great caution and in the presence of hydrochloric acid, otherwise the tin will be partly precipitated as the insoluble metastannic acid.

Ferric chloride (Fe_2Cl_6) oxidises stannous chloride to stannic chloride. If the ferric chloride is previously mixed with potassium ferricyanide, the addition of stannous chloride to the solution at once gives a dark blue precipitate of Prussian blue or a similar compound.*

Mercuric chloride ($HgCl_2$) gives with an excess of stannous chloride a white precipitate of mercurous chloride (Hg_2Cl_2) which soon changes to a dark coloured precipitate of metallic mercury. If the reagent is added in excess the white mercurous chloride alone is produced.*

Gold chloride ($AuCl_3$) gives a purple precipitate of the so-called " purple of Cassius," especially in the presence of a third substance, such as ferric chloride or nitric acid, which improves the colour. The precipitate may be regarded as a compound of gold with stannic dioxide ($Au_2 + 3SnO_2$), or as a compound of aurous and stannous stannates ($Au^I_2Sn^{IV}O_3$, $Sn^{II}Sn^{IV}O_3$).

The solution of stannic chloride for the following reactions should be prepared from stannous chloride by means of potassium chlorate as described above.

Sulphuretted hydrogen (H_2S) gives with acid solutions of

stannic salts a yellow precipitate of stannic sulphide (SnS_2) which is insoluble in dilute acids, soluble on heating in strong hydrochloric acid, soluble also in ammonium sulphide and in caustic soda being reprecipitated in each case on acidification.* It is soluble, though with difficulty, in ammonia, but not soluble in ammonium carbonate. Nitric acid attacks it with formation of the insoluble metastannic acid. The compounds produced when the sulphide is dissolved in alkalies or alkaline sulphides are analogous to those given above in connection with stannous sulphide.

Ammonium sulphide (Am_2S) gives the same precipitate soluble in excess.

Sodium hydrate (NaOH) gives a white precipitate of stannic acid (H_2SnO_3) readily soluble in excess forming sodium stannate (Na_2SnO_3).*

Ammonia (AmOH), *ammonium carbonate* (Am_2CO_3) and *sodium carbonate* (Na_2CO_3) give similar precipitates,* but do not dissolve them in excess to more than a slight extent.

From a solution of stannic chloride containing *as little free acid as possible*, dilute sulphuric acid or solutions of many salts such as sodium sulphate and ammonium nitrate, precipitate stannic acid, especially on dilution, though probably always mixed with metastannic acid.

When strong nitric acid acts upon metallic tin or some of its compounds a white insoluble precipitate of metastannic acid is produced.* A dilute solution of stannic chloride after some time shows the characteristic reactions of metastannic acid.

The changes that take place when stannic acid and metastannic acid change the one into the other are not understood, but the two acids may be distinguished by various properties. In the presence of tartaric acid am-

monia precipitates metastannic acid but not stannic acid from acid solutions. Metastannic acid is not soluble in strong hydrochloric acid, but the compound formed by its action is soluble in water though not in dilute acids. Metastannic acid is precipitated by caustic soda from moderately dilute acid solutions and not dissolved in excess, while stannic acid is dissolved in excess. Metastannic acid is insoluble in dilute hydrochloric acid, sulphuric acid, and nitric acid, while ordinary stannic acid is soluble in any of these. Strong hydrochloric acid slowly converts metastannic into ordinary stannic acid, especially on heating. By fusion of metastannic acid with caustic alkalies ordinary stannates result.

Metallic tin is easily precipitated by zinc from slightly acid solutions of its salts, in the form of a spongy deposit. The tin so obtained is soluble in hydrochloric acid, though rather slowly, forming stannous chloride.* Stannic chloride is reduced to stannous chloride by boiling it in solution with metallic copper.

Antimony

Use antimonious oxide (Sb_2O_3) and potassium pyro-antimonate [1] ($K_2H_2Sb_2O_7,6H_2O$).

Compounds of antimony when heated on charcoal with a flux of fusion mixture and potassium cyanide are reduced, and a bead of metallic antimony is obtained that is so volatile that dense fumes of oxide rise during the heating and even after the flame is withdrawn. If not interfered with by draughts, as the metal cools the oxide will form crystals on and around the bead. The incrustation is white.*

To confirm the following reactions, some oxide of antimony should be dissolved in hydrochloric acid, and

---

[1] This is the salt commonly known as potassium metantimonate.

the solution diluted as much as possible without causing the precipitation of the oxychloride.

Sulphuretted hydrogen (H_2S) gives from solutions of antimonious salts an orange red precipitate of antimonious sulphide (Sb_2S_3). The precipitate is soluble in alkaline sulphides forming thioantimonites, and in caustic soda forming a mixture of the thio- and oxy-antimonites, and and from these solutions the sulphide is reprecipitated on acidification.* It is insoluble in dilute acids, but soluble in strong hydrochloric acid. It is slightly soluble in ammonia and insoluble in ammonium bicarbonate.

Ammonium sulphide (Am_2S) gives the same precipitate soluble in excess of the reagent.

Sodium hydrate (NaOH) gives a white precipitate of antimonious oxide (Sb_2O_3) readily soluble in excess with formation of sodium antimonite ($NaSbO_2$).* From a solution of tartar emetic ($K(SbO)C_4H_4O_6$) the precipitate obtained dissolves more easily in excess of caustic soda. The previous addition of an alkaline tartrate (such as Rochelle salt) prevents the precipitation. The addition of a solution of an alkaline tartrate after the precipitate is obtained dissolves a part but not the whole of it.

Ammonia (AmOH) gives the same precipitate not soluble in excess of the reagent.* With a solution of tartar emetic the precipitate appears more slowly. Alkaline tartrates behave in this as in the previous case.

Sodium carbonate (Na_2CO_3) gives the same precipitate,* soluble in a large excess of the reagent on warming, but the solution speedily becomes turbid again, especially on cooling. With tartar emetic the precipitate obtained is not soluble in excess. Alkaline tartrates behave as before in preventing the precipitation if added first, and partially dissolving it if added afterwards.

Water (H_2O) gives a white precipitate of antimonious

oxychloride (SbOCl) which is soluble in hydrochloric acid. It is also soluble in tartaric acid,* and from a solution of tartar emetic water gives no precipitate. Bismuth oxychloride is not soluble in tartaric acid.

Metallic zinc, and many other metals, precipitate metallic antimony from solutions of its salts as a black powder. A more characteristic and delicate reaction consists in putting the solution into a platinum capsule, or into a dish with a piece of platinum foil, and then introducing a piece of zinc so that it touches the platinum. The antimony is then deposited on the platinum as a black stain.* Tin under similar conditions is not precipitated on the platinum but on the zinc. The stain does not disappear on warming it with dilute hydrochloric acid, but is readily removed by dilute nitric acid on warming. For this reason the solution should be free from nitric acid.

Antimonious compounds are easily oxidisable, especially in alkaline media, to antimonic compounds or antimonates. The antimonates of many metals are known.

Nitric acid acts readily on metallic antimony and gives the tetroxide, Sb_2O_4 (or SbO_2), which is somewhat analogous to the hydrated dioxide of tin (metastannic acid) obtained by the action of nitric acid on tin. Sb_2O_4 is the most stable oxide of antimony at a high temperature in presence of air. Antimonic anhydride is the pentoxide (Sb_2O_5), and the antimonic acids are hydrated compounds of it.

Auric chloride ($AuCl_3$) gives with a solution of antimonious chloride in hydrochloric acid a yellow precipitate of metallic gold, especially on heating, which is mixed with a white precipitate of antimonic acid, unless the solution contains a considerable excess of hydrochloric acid. The oxidation of the antimonious to the antimonic compound here is effected in an acid solution.

Silver nitrate (AgNO₃), if added to a solution of antimonious oxide in caustic soda, gives a brownish black precipitate, and if ammonia is then added, a black insoluble residue appears of a mixture of metallic silver and antimony.* The oxide of silver formed by the action of the caustic soda on the silver salt gives up a part of its oxygen to the antimonious compound. The exact character and composition of the substance that remains insoluble in ammonia is not known. With an antimonate the silver oxide is not reduced, and it remains soluble in ammonia.

Hydrochloric acid (HCl) gives from a solution of potassium pyroantimonate a white precipitate of antimonic acid (HSbO₃ ?), which is readily soluble in excess of the acid.*

The five following reactions refer to a solution of antimonic acid in hydrochloric acid.

Sulphuretted hydrogen (H₂S) gives an orange red precipitate of antimonic sulphide (Sb₂S₅),* but a part of the precipitate decomposes into antimonious sulphide and sulphur, thus:—

$$Sb_2S_5 = Sb_2S_3 + S_2.$$
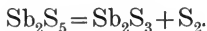
The precipitate therefore is a mixture of antimonic sulphide, antimonious sulphide and sulphur. It is soluble in alkaline sulphides to form thioantimonates, and in caustic soda to form a mixture of oxy- and thio-antimonates. It is even soluble in ammonia, for antimonious sulphide is soluble in ammonia in the presence of sulphur sufficient to transform it into antimonic sulphide. From these solutions the sulphide is reprecipitated on acidification. It is sparingly if at all soluble in hydrogen ammonium carbonate. It is readily soluble in hot strong hydrochloric acid, with deposition of sulphur.

Ammonium sulphide (Am_2S) gives the same precipitate soluble in excess of the reagent.

.. *Sodium hydrate* (NaOH) gives a white precipitate of antimonic acid, soluble on warming with excess of the reagent.* It must be remembered that sodium pyro-antimonate is a sparingly soluble salt, but this fact is not likely to interfere with this reaction.

Ammonia (AmOH) gives a similar precipitate,* slightly if at all soluble in excess.

Sodium carbonate (Na_2CO_3) gives a similar precipitate * quite perceptibly but not completely soluble in excess of the reagent.

Antimonic compounds are not reduced by ferrous sulphate. They are reduced by stannous chloride to antimonious compounds, and by nascent hydrogen giving the metal, and even partly to antimonuretted hydrogen (SbH_3). A solution of antimonic acid in hydrochloric acid liberates iodine from a solution of potassium iodide. In the absence of other substances that set iodine free, a small quantity of antimonic acid may be recognised by this reaction, especially if starch is added to the iodide solution. Solutions of antimonious salts do not show this reaction.

The detection of antimony by the formation of anti-monuretted hydrogen and its reactions is considered in conjunction with the detection of arsenic by the same methods in the next section.

Arsenic

Starting with the most positive metals, potassium and sodium, we have passed to other metals that could be reduced to the metallic state with facility, and have noticed that some of them could act when highly oxidised as the acid instead of the basic radical of salts. Tin

shows a marked tendency to lose its basic character in stannous as well as stannic compounds, antimony inclines still more strongly in this direction, and arsenic goes still further. In almost all arsenic compounds the element plays an acidic and not a basic part. Moreover in passing from antimony to arsenic we pass from a true metal to a non-metal, though arsenic can hardly be classed with the other non-metals for practical purposes. Although the element arsenic is not a metal, or it may be called an imperfect metal, it is convenient to consider it in this place as if it were a metal, because of the intimate relationship that exists between antimony and arsenic, and chiefly because it so readily forms a sulphide by the action of sulphuretted hydrogen. The most of the reactions by which arsenic is identified are therefore of a different character from those of the metals previously considered.

Use arsenious anhydride (As_2O_3) or potassium arsenite (K_3AsO_3), or potassium arsenate (K_3AsO_4) as directed. In the following experiments very small quantities should be employed, and it is desirable to avoid inhaling the poisonous fumes.

It is important also that the tubes and the substances used are dry, as if water is given off on heating it will probably interfere with the satisfactory deposition of the sublimates. If a little water is given off it should be removed with a small roll of filter paper before the heating is continued.

Arsenious anhydride (As_2O_3) is readily volatile : a little should be heated in a bulb tube. It fuses slightly if at all, and gives a white sublimate.* Where it condenses slowly, as perhaps in the heated bulb of the tube itself after it is removed from the flame, it will be seen to form distinct crystals with triangular faces.

Heated with charcoal powder or potassium cyanide, preferably mixed with sodium carbonate (in the case of the sulphide the charcoal powder is of very little use), most arsenic compounds give a sublimate of the element as a black mirror-like deposit, a garlic or oniony odour being given off at the same time.* If the sublimate is small in quantity it may be further identified by breaking the bulb off the tube and holding the tube, which is now open at both ends, slopingly over the flame, so that the arsenic is gently heated and the draught through the tube carries the vapour slowly along. The arsenic will be oxidised and partially deposited on the cool part of the tube in the form of white shining octahedra, the shape of which will be clearly visible through a magnifying glass. The presence of reducible metals, such for example as lead, copper or iron, in sufficient quantity, prevents the sublimation of the reduced arsenic by combining with it. The action of the potassium cyanide in this reaction is to combine with the oxygen or sulphur previously combined with the arsenic, forming the cyanate or thiocyanate, (KCNO or KCNS).

When very small quantities of arsenic compounds have to be dealt with a tube of small capacity must be used, or the element will not be obtained in the free condition, but will be oxidised by the air in the tube. To still further improve the conditions, a tube open at both ends may be used, and a slow current of carbonic anhydride passed through it to exclude air. The tube may be narrowed where the arsenic is condensed, that it may be concentrated on a smaller surface and so be more obvious.

Some arsenites when heated alone give a sublimate of arsenic. Sodium arsenite does, leaving a residue of sodium arsenate, one portion of the arsenious acid radical

oxidising another portion to the arsenic acid radical, itself being reduced to the elementary condition.

Heated on charcoal arsenic compounds give a characteristic garlic odour,* which is stated to be due to a suboxide.

Sulphuretted hydrogen (H_2S) gives, with an acidulated solution of arsenious anhydride or an arsenite, a bright yellow precipitate of arsenious sulphide (As_2S_3). The precipitate is readily soluble in alkalies, alkaline sulphides,* alkaline carbonates, and even in alkaline bicarbonates, forming arsenite with the thioarsenite, or the latter alone according to circumstances. Sulphide of arsenic has more of the characters of an anhydride than the sulphides of tin or antimony. From any of these solutions the arsenious sulphide is reprecipitated by acidification. The sulphide is insoluble in boiling strong hydrochloric acid, but soluble in nitric acid. It is soluble on warming in a solution of potassium hydrogen sulphite with excess of sulphurous acid, potassium arsenite and thiosulphate being produced, thus:—

$$2As_2S_3 + 16HKSO_3$$
$$= 4KAsO_2 + 6K_2S_2O_3 + S_3 + 7SO_2 + 8H_2O.$$
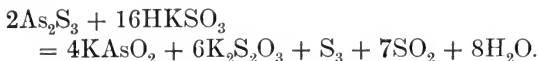
Ammonium sulphide (Am_2S) gives the same precipitate soluble in excess of the reagent.

Alkalies give no precipitates with arsenious compounds. Indeed, arsenious anhydride is more soluble in alkaline solutions than in water or in hydrochloric acid. The acidification of the solution of an arsenite does not generally precipitate the anhydride, but—

Hydrochloric acid (HCl) gives a white precipitate of arsenious anhydride from strong solutions of alkaline arsenites.

Silver nitrate ($AgNO_3$) gives from a solution of an arsenite

a yellow precipitate of silver arsenite (Ag_3AsO_3), which is easily soluble in either ammonia or nitric acid.* It is also soluble in ammonium salts, so that if a very small quantity has been dissolved, it is not reprecipitated on neutralisation. Silver nitrate when added to an aqueous solution of arsenious anhydride gives hardly any precipitate, but the precipitate appears on cautiously adding ammonia which of course neutralises the arsenious acid forming ammonium arsenite.

Copper sulphate ($CuSO_4$) gives a light green precipitate of hydrogen cupric arsenite ($HCuAsO_3$), called Scheele's green.* This also is soluble in either nitric acid or ammonia, ammonia giving a colourless solution, if an excess of the reagent is avoided, the copper being reduced to the cuprous condition by the arsenious acid. But a colourless solution cannot be obtained without special care to exclude air, because the ammoniacal solution of cuprous oxide oxidises so very rapidly in contact with air.

Metallic copper, which should be clean, if put into a solution of an arsenite acidified with hydrochloric acid precipitates the arsenic, which deposits upon and combines with the surface of the copper, forming a grey coating. If there is much arsenic the film peals off in scales, or it may be detached by heating with ammonia. With weak solutions of arsenic heating facilitates the reaction. The scales, or the copper with the deposit upon it, should be introduced into a glass tube and heated. Some of the arsenic is given off, and, being oxidised by the air in the tube, forms a sublimate of the characteristic crystals of arsenious anhydride.* This use of metallic copper constitutes Reinsch's test for arsenic.

Arsenious compounds are easily oxidised to arsenic compounds even in solution. Nitric acid, aqua regia, chlorine and the hypochlorites, readily effect the change. Arsenious

anhydride dissolved in hydrogen sodium carbonate is oxidised with formation of an alkaline arsenate by iodine, which is conveniently dissolved in potassium iodide solution.

Silver nitrate ($AgNO_3$) added to a solution of arsenious anhydride in excess of ammonia gives no precipitate at first, but on boiling metallic silver separates,* and an arsenate is formed.

Auric chloride ($AuCl_3$), with an acid solution of arsenious anhydride, gives a precipitate of metallic gold, the arsenious being oxidised to arsenic acid.

Copper sulphate ($CuSO_4$), if added to a strongly alkaline solution of an arsenite, gives on warming a red precipitate of cuprous oxide (Cu_2O),* the arsenite being oxidised to arsenate.

For the following reactions, use a solution of an alkaline arsenate.

Sulphuretted hydrogen (H_2S) affects an acidulated solution of an arsenate so slowly that there is danger of overlooking the slight precipitate altogether. By working with a hot solution the precipitate forms more readily,* but its production is slow at the best, and after several hours it may not be complete. The precipitate consists of arsenious sulphide and sulphur ($As_2S_3 + S_2$). It dissolves as a whole in alkalies and alkaline sulphides, forming thioarsenates or thio-arsenates with oxy-arsenates. Acids reprecipitate the sulphide, thioarsenates yielding, however, thioarsenic acid (H_3AsS_4). The original precipitate is shown to be a mixture of arsenious sulphide and sulphur by the fact that weak ammonia dissolves out arsenious sulphide from it and leaves the sulphur, and carbon disulphide dissolves the sulphur and leaves the arsenious sulphide. If the arsenate is first reduced to the arsenious condition, and this is quickly done by means of sulphurous

acid or an alkaline sulphite in an acid solution, then the arsenic is rapidly precipitated as already stated.

Hydrochloric acid (HCl) does not precipitate the acid from even strong solutions of alkaline arsenates.

Silver nitrate ($AgNO_3$) gives a reddish brown precipitate of silver arsenate (Ag_3AsO_4) soluble in either ammonia or dilute nitric acid,* and not reprecipitated on neutralisation if there is only a little of it, as it is somewhat soluble in ammonium salts.

Copper sulphate ($CuSO_4$) gives a light greenish blue precipitate of hydrogen cupric arsenate ($HCuAsO_4$),* soluble in either nitric acid or ammonia.

Magnesia mixture, that is a solution of magnesium sulphate or chloride mixed with ammonium chloride and ammonia, gives a white crystalline precipitate of ammonium magnesium arsenate ($AmMgAsO_4$).*

Many other solutions of metallic salts give precipitates of arsenates of the metals used, arsenic acid behaving in this matter very much like phosphoric acid.

Ammonium molybdate (Am_2MoO_4), with excess of nitric acid, gives a yellow precipitate of ammonium arseno-molybdate, especially on warming; * in this reaction also arsenates behave like phosphates.

Reinsch's test succeeds with arsenates as with arsenites, but the solution is preferably more strongly acid and kept hot.

Marsh's test for arsenic and antimony.—When an acid (nitric acid should be avoided) solution of an arsenic or an antimony compound is introduced into a generator in which hydrogen is being prepared from zinc and a dilute acid, such as sulphuric, a part of the arsenic or the antimony combines with the hydrogen to form arsenuretted or antimonuretted hydrogen, thus:—

$$As_2O_3 + 6H_2 = 3H_2O + 2AsH_3.$$
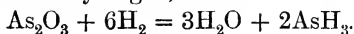
Arsenuretted hydrogen is exceedingly poisonous, and only small quantities of the arsenic or antimony solutions should be employed. There is no disadvantage in this, for the reaction is so delicate that the arsenic present in ordinary zinc and sulphuric acid can easily be detected. For this reason it is necessary to first test the reagents to be used to see that they are free from arsenic, before the finding of arsenic can be accepted as proof of its presence in the substance tested. This is not an exceptional reaction, for sulphuretted hydrogen and other similar compounds can be produced in a similar manner; it is, however, a kind of reaction that more frequently occurs in connection with the non-metals than the metals, and antimony in this as well as in other reactions shows how nearly related it is to the non-metals.

Arsenuretted and antimonuretted hydrogen burn with blue flames; and if a cold surface, such as that of a piece of porcelain, is depressed into the flame, a dark coloured spot of the separated element is produced. The antimony deposit is a lustreless black, the arsenic deposit being of a brownish black colour and inclined to be shiny. The formation of these deposits is analogous to the deposition of soot under similar conditions when a compound of hydrogen with carbon is burned, as in a candle flame. If there is only a small quantity of arsenic or antimony present, the porcelain may be held in the flame for a considerable time, and the deposit will increase; and to keep the porcelain cool, a small dish containing water may be used, the flame impinging on the outside. These deposits, or spots, or "mirrors" as they are sometimes called, can be easily distinguished by chemical means. A solution of sodium hypochlorite applied to the spot dissolves it quickly if it is arsenic, very slowly indeed if it is antimony; indeed, no visible change occurs in the antimony

deposit during the time that would usually be devoted to the test.

A better method than the above is to allow the hydrogen with which is mixed the compound gas to pass through a drying tube filled with calcium chloride, and then through a tube that is heated to redness at one part by a single flame. If the tube is narrowed down about an inch beyond the heated part, the deposit will be more clearly seen if it is small. The heating decomposes the gas, and the arsenic or the antimony will be deposited on the cooler part of the tube as an adherent film. This modification of the test has the advantage that the operation can be kept going for a long time, and the deposit allowed to accumulate.

To distinguish an antimony from an arsenic deposit in the tube, if it is in not too small a quantity, the mirror may be gently heated while the hydrogen continues to pass. Arsenic will impart a garlic odour to the escaping hydrogen, antimony will volatilise less readily and fuse into small globules visible through a lens.

A better method is to pass a very slow current of sulphuretted hydrogen through the tube, very gently heating the deposit. If both metals are present, the more volatile arsenious sulphide will appear by the side of the less volatile red (or black if in thick layers) antimonious sulphide.

A current of dry hydrochloric acid passed through the cold tube will cause the antimony deposit to disappear entirely, the sulphide being converted into chloride and volatilised. By condensing the hydrochloric acid in water the antimonious chloride may be detected in the ordinary manner. The arsenious sulphide remains in the tube ; and if further proof of its identity is wanted, it may be dissolved in hydrogen ammonium carbonate and the solution examined in any suitable manner.

These two gases may be identified even if mixed by passing them into a solution of silver nitrate. The arsenuretted hydrogen is oxidised to arsenious acid, metallic silver being precipitated, thus:—

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3.$$
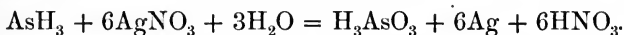
while the antimonuretted hydrogen forms silver antimonide, thus;—

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3.$$
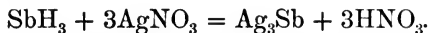
A precipitate is formed in any case, but the antimony is in the precipitate while the arsenic is in the solution. By carefully neutralising the solution with ammonia a yellow precipitate of silver arsenite will be obtained if there is excess of silver nitrate present. The antimony may be detected in the residue by boiling it with tartaric acid and passing sulphuretted hydrogen through the solution so obtained.

It should be noticed that in the above reactions it is always the superior oxidisability or acid character of arsenic that is made use of. The sodium hypochlorite oxidises the arsenic, and not the antimony. The hydrochloric acid attacks the antimonious sulphide and not the arsenious sulphide, the antimony sulphide being of a more basic character than the other. The silver nitrate oxidises the arsenious compound, but only oxidises the hydrogen of the antimonuretted hydrogen, leaving the metal unoxidised, mixed or combined with the deposited silver.

COMPARATIVE REMARKS ON THE REMAINING MEMBERS OF GROUP II.—THE SECOND SECTION

(TIN, ANTIMONY, AND ARSENIC)

The compounds of these elements yield the corresponding sulphides by passing sulphuretted hydrogen through acid solutions of them, like those of the metals of the first section of this group, but they differ from them in forming sulphides soluble in alkalies or alkaline sulphides.

As remarked already, the tendency for the ordinary oxides and sulphides of tin, antimony and arsenic, to behave as anhydrides, is more marked than is the case with the oxides of any of the metals previously considered. As usual, too, the higher oxides and the higher sulphides are more distinctly acid in character than the lower; that is, they combine with (or dissolve in) alkalies more readily and with acids less readily than the lower and more basic compounds. Stannic sulphide is more easily soluble in alkalies than stannous. Arsenious sulphide is of all (arsenic sulphide we have very little to do with) the most soluble in alkalies and least soluble in acids. It is soluble in hydrogen ammonium carbonate, which will not dissolve any other of the sulphides, and does not dissolve in hydrochloric acid, which dissolves all the others.

Tin in its compounds presents no very striking reactions; it is generally recognised by the reducing power of stannous compounds, or by the production of metastannic acid by the action of nitric acid.

Antimony is exceptional in the formation of its oxychloride with great facility, almost equalling bismuth. It differs from bismuth in the solubility of its oxychloride in tartaric acid. Even the finely divided metal itself as obtained by precipitation is soluble on boiling it in a

solution of tartaric acid. It resembles tin in giving an insoluble white oxide (or hydrate) by the action of nitric acid ; and here again the antimony compound is distinguished from the other by its solubility in tartaric acid.

Arsenic is distinguished, as has already been remarked, by its acid character when in combination. Arsenic acid is so similar to phosphoric acid that it is hardly distinguishable from it except by reducing it to a less highly oxidised compound. It is also noted for its volatility, comparing with mercury salts in this, arsenic, mercury and ammonium being the three most volatile bases of those considered. Many other comparisons have been made between the compounds of these elements in giving their reactions, as between arsenuretted and antimonuretted hydrogen, &c.

Separation.—Arsenic may be separated from tin and antimony by taking advantage of the insolubility of its sulphide in strong boiling hydrochloric acid, or the solubility of its sulphide in hydrogen ammonium carbonate.

The carbonate must of course not be heated too much or it will lose carbonic acid, and will then not be without action on the other sulphides (antimonious and stannic). Arsenious sulphide is also soluble in a solution of hydrogen potassium sulphite with excess of sulphurous acid, while the other sulphides are insoluble. Arsenic acid may be produced by several methods, and it may then be separated by precipitation with magnesia mixture.

By introducing compounds of these three elements into a hydrogen apparatus and passing the evolved gases through silver nitrate solution, the arsenic alone (that is some of it) is obtained in the solution in the form of arsenious acid. Some of the antimony is precipitated in the metallic state in the silver nitrate solution, and the

tin remains in the generator, being precipitated as metal. The tin may be dissolved in hydrochloric acid and the stannous chloride recognised by its action on mercuric chloride. The residual antimony and arsenic (if any) in the generator will not interfere with this test.

Antimony may be separated from arsenic and tin by oxidising their sulphides or other compounds with concentrated nitric acid, evaporating, and fusing the residue with excess of caustic soda. Sodium pyro-antimonate, stannate and arsenate are produced, and by treating with water and adding afterwards some alcohol, the sodium pyroantimonate alone is left insoluble.

Tin can be separated from arsenic and antimony by treating their sulphides with concentrated nitric acid, which dissolves the arsenious sulphide, forming arsenic acid, and leaves the tin as metastannic acid, and the anti-mony (or the most of it) as tetroxide. Heating with tar-taric acid will dissolve the antimony oxide. The remaining metastannic acid may be reduced to the metal by drying it and heating it with potassium cyanide, and the metal may be identified by any of its reactions. Stannic sul-phide is soluble under certain conditions in a very strong solution of oxalic acid, the sulphides of antimony and arsenic being insoluble. But the precautions necessary to ensure success by this method are such that it is not to be recommended.

By adding sodium thiosulphate in excess to a boiling hydrochloric acid solution containing salts of tin, arsenic, and antimony, the sulphides of arsenic and antimony are precipitated, and the tin remains in solution. This method is not worthy of special recommendation, because, in the absence of hydrochloric acid sulphide of tin would also be precipitated, and if much acid is present it retards the precipitation of the antimony sulphide.

Other methods for detecting these metallic radicals in the presence of each other have been given. Among them the stain on platinum produced by solutions containing antimony when platinum and zinc are in contact in the solution, and Reinsch's test, may be specially mentioned.

The student should practise the separation of the members of Group II., including Group I., according to the table given at page 174, before proceeding to the reactions of the acid radicals.

THE ACID RADICALS.

THE reactions of this group of bodies are often, indeed generally, referred to as the reactions of the acids. Although in some cases the acids—that is the hydrogen salts—do give the changes described, yet the reactions given apply to salts in general, and not only or specially to the hydrogen salts. To take an example, the acid radical of sulphates may be regarded as SO_4, and what is commonly referred to as the detection of sulphuric acid is really the detection of such a group in compounds.

As there is no perfect conception of the constitution of salts that finds general acceptance, and the most common nomenclature is a relic of old theories, which, though still often useful, have been found insufficient, it is not easy to find a system of nomenclature that is free from objection. To exactly express what is intended requires lengthy circumlocutory phrases that it would be impossible to use without distracting attention from the facts under consideration. Our present nomenclature is at best a compromise. When referring to the reactions of carbonates or sulphates, for example, it is not the reactions of these *salts* that are specially referred to, but those of their properties that are particularly associated with the acid radical they contain.

It is not possible to divide the acid radicals into groups in a precise and useful manner similar to that adopted

for the basic radicals, and, as will be seen later, such a classification, if it were possible, would rarely be advantageously applied in practical analytical operations.

It should be noticed that the properties of the acid radicals (in compounds, of course) do not appear to be so intimately connected with the characteristic elements they contain, such as carbon or sulphur, as the properties of the metallic radicals are with the metals themselves. This is probably due partly to the larger proportion of oxygen in the acid radicals, for when there is no oxygen present, as in the binary compounds (sulphides, chlorides, &c.), the difference nearly or entirely disappears.

In those cases in which several substances are mentioned, it will be sufficient for the student, when confirming the reactions, to take one only as an example.

Carbonates

The normal carbonates have the general formula M'_2CO_3, in which M' stands for a monad metal.

When heated in a glass bulb tube, potassium, sodium, barium, strontium, and calcium normal carbonates are very slightly, if at all, decomposed. The alkaline carbonates fuse. Calcium carbonate is decomposed at a red heat into carbonic anhydride and lime. Barium and strontium carbonates require a higher temperature for their decomposition. Ammonium carbonate volatilises entirely with decomposition, giving a sublimate. All other carbonates are decomposed on ignition, giving off carbonic anhydride, and leaving the oxide of the metal unless the oxide of the metal is also decomposed. Silver and mercury carbonates give off carbonic anhydride and oxygen, leaving the metal. The mercury oxide is not completely decomposed. Acid (or bi-) carbonates evolve carbonic anhydride at a low temperature, even by

heating them in solution in water, and the carbonic anhydride evolved can be detected as stated below.

Dilute acids in general (hydrochloric or sulphuric) cause effervescence when poured upon carbonates, due to the escape of carbonic anhydride. The gas is identified by (1) the effervescence ; (2) its being colourless ; (3) its very slight odour (probably not perceptible) ; (4) its action upon lime or baryta water to give a white precipitate. There is no need to use a delivery tube to conduct the gas into the lime water ; it is better to allow the gas to accumulate in the upper part of the tube in which the decomposition is taking place, then to pour the gas, just as if it were a visible liquid, into another tube that contains about one-sixth of its capacity of lime water. The gas is considerably heavier than air, and can easily be poured. Then close the second tube with the thumb and shake it.* Many minerals, such as spathic iron ore and magnesite, must be warmed with the acid before they are acted upon. An excess of carbonic anhydride will dissolve the barium or calcium carbonate first precipitated, forming the bicarbonate. By heating the solution the excess of carbonic anhydride is driven off, and the precipitate is obtained again.

To detect a small amount of carbonate in a solid substance, such as a mineral, boil a gram or two of the powdered material with water in a test tube until the air is driven out from the water ; let the substance settle for a few seconds, then pour a little strong hydrochloric acid carefully down the inclined tube, and look attentively for bubbles in the liquid at the upper side of the tube. Cold water dissolves its own bulk of carbonic anhydride, so that a little gas evolved in a cold solution may produce no visible bubbles, and so pass unnoticed.

Nitrites, sulphites, and some sulphides give off gases

when treated with dilute acids. If either of these is present, *potassium bichromate* may be used instead of an acid, and then carbonic anhydride alone will be evolved. The substance is covered with water, a small lump of the bichromate added, and the mixture warmed.* The test is completed as above. It is especially necessary to notice that sulphurous anhydride given off by dilute acids from sulphites precipitates lime or baryta water, just as carbonic anhydride does. The bichromate in this test oxidises the sulphites and sulphides to non-volatile compounds, sulphates or sulphur, and nitrites are not decomposed by it.

If carbonic anhydride has been evolved mixed with any of the gases just mentioned, before testing for it the mixture of gases may be passed through a solution of potassium dichromate acidified with sulphuric acid, or through bromine water, or, to remove sulphuretted hydrogen, through a solution of copper sulphate.

The carbonates of the alkalies and the acid carbonates of these and some other metals are soluble in water, the rest are insoluble. The alkaline carbonates show a strong alkaline reaction to litmus paper.

To remove carbonic acid from a solution of an alkaline carbonate for analytical purposes, *calcium chloride* ($CaCl_2$) or *barium chloride* ($BaCl_2$) is generally employed. Either of them gives a white precipitate of the carbonate of the metal.

Sulphates

The normal sulphates have the general formula M'_2SO_4, in which M' stands for a monad metal.

Heated in a bulb tube, the normal sulphates of the alkalies, alkaline earths and lead, and one or two others, are not decomposed. The sulphates of most of the heavy

metals are decomposed and give off sulphuric or sulphurous anhydride, or both, sometimes oxygen too, leaving the oxide. The decomposition of ferrous sulphate is notable as it leaves red ferric oxide, thus :—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$
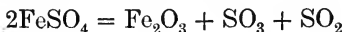
Ammonium sulphate breaks up altogether, giving off sulphurous anhydride, ammonia, nitrogen and water. Some of the hydrogen of the ammonium group is oxidised by the oxygen of the acid radical; of course a sublimate is obtained. The acid (or hydrogen or bi-) sulphates of potassium and sodium fuse readily and give off sulphuric acid, which condenses in drops on the cool part of the tube.

Heated on charcoal with sodium carbonate or fusion mixture, sulphates form the alkaline sulphate; and this, when fused so that it sinks into the hot charcoal, or if heated in the reducing flame, is reduced to sulphide. If the residue is placed on a clean surface of silver (a silver coin serves) and moistened with water, the silver is stained black, silver sulphide being formed.* This reaction is not peculiar to sulphates, for any sulphur compound will give it, sulphites and obviously sulphides even more readily than sulphates.

Neither dilute nor concentrated acids have any visible effect upon sulphates.

Sulphates are soluble in water, except those of barium, strontium, calcium and lead, and a few basic salts. Calcium and lead sulphates dissolve with fair ease in hydrochloric acid. Barium and strontium sulphates are most readily attacked by fusion with fusion mixture, which converts them into carbonates. An alkaline sulphate is formed in which the acid radical is easily detected. Boiling with a strong solution of sodium carbonate will decompose them ;

but this is a tedious and rarely necessary operation. By heating them with carbonaceous matter they can be reduced to sulphides which are attacked readily by dilute acids; but this process is not generally suitable for analytical work.

Barium chloride ($BaCl_2$) added to a solution of a sulphate gives a white precipitate of barium sulphate ($BaSO_4$) which is insoluble in hydrochloric acid or on boiling.* Dilute hydrochloric acid should be added before the reagent to prevent carbonates, chromates, &c., from giving precipitates. Strong hydrochloric acid should not be used as it will give a crystalline precipitate of barium chloride itself, this salt being less soluble in hydrochloric acid than in water. Exceedingly dilute solutions of sulphates give a precipitate with barium salts only on standing. For further details concerning the properties of barium sulphate, see the section on Barium. There are no other compounds than sulphates that give a precipitate under the conditions named except hydrofluosilicic acid and its soluble salts.

To detect free sulphuric acid in solution with a sulphate, a little cane sugar is added and the solution evaporated to dryness on a water bath. The sugar in the residue is blackened by the free sulphuric acid as it gets concentrated by the evaporation.

Sulphites

The normal sulphites have the general formula M'_2SO_3, in which M' stands for a monad metal.

Sulphites resemble carbonates in several of their reactions, sulphurous and carbonic anhydrides having many properties in common. But sulphites can be oxidised to sulphates or reduced to sulphides, and carbonates present no changes analogous to these.

Heated in a bulb tube, some sulphites give off sulphurous anhydride, leaving the base as oxide. Others, especially the alkaline sulphites, oxidise themselves, a part of course being reduced, forming a sulphide and sulphate, thus :—

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

Sulphuretted hydrogen is given off on adding a little dilute acid to the residue.*

Heated on charcoal with fusion mixture, sulphites give the same reaction as sulphates, but rather more readily.

Dilute acids (hydrochloric or sulphuric) liberate sulphurous anhydride from sulphites, and this gas behaves towards lime or baryta water exactly as carbonic anhydride does.* It differs from carbonic anhydride in having a pungent odour (familiar as the odour of burning sulphur) and in coming off with very little or no effervescence. Sulphurous anhydride is very much more soluble in water than carbonic anhydride, so that when liberated it may remain chiefly in solution. Potassium bichromate does not liberate sulphurous anhydride from sulphites, but oxidises them to sulphates.

The solubility of sulphites in water is analogous to that of carbonates. The alkaline sulphites and some acid salts are soluble. The acid (or bi-) sulphites of the alkaline earths are decomposed on boiling their solutions, sulphurous anhydride being given off and the sulphite of the metal precipitated.

Use for the following reactions a solution of sodium sulphite ($Na_2SO_3,7H_2O$).

Barium chloride ($BaCl_2$) gives with solutions of normal sulphites a white precipitate of barium sulphite ($BaSO_3$) which, like the carbonate, is easily soluble in dilute hydrochloric acid. But any of the more usual oxidisers,

such as sodium hypochlorite, chlorine water, nitric acid, potassium permanganate, &c., oxidise the soluble sulphite into the insoluble sulphate.* The oxidation is so readily effected that exposure to air will materially interfere with the solution of barium sulphite. Most sulphites are already partly oxidised, and the precipitate given by barium chloride in that case is a mixture of sulphite and sulphate, and therefore does not dissolve completely in hydrochloric acid. The acid solution of the sulphite may be filtered off from the remaining sulphate, then, on adding an oxidising reagent to the solution, the sulphite is oxidised and the sulphate is precipitated.

Silver nitrate ($AgNO_3$) gives a white precipitate of silver sulphite (Ag_2SO_3) which is soluble in excess of the alkaline sulphite. On heating the precipitate in the liquid it darkens, owing to the formation of metallic silver,* thus:—

$$Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4.$$
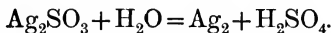
An excess of the alkaline sulphite very much retards the reduction on heating, and, if the silver is slowly deposited it may attach itself to the glass tube and form a brilliant mirror. Particular notice should be taken of this reaction as it is typical of the effect of sulphites and thiosulphates on the salts of many of the heavy metals, though the change is often varied in some detail.

Mercurous nitrate ($Hg_2N_2O_6$) gives a grey precipitate of metallic mercury, whether the sulphite or the mercury salt is in excess. By boiling the precipitate with strong hydrochloric it soon coalesces into globules.*

Mercuric chloride ($HgCl_2$) added in excess gives on heating a white precipitate which is not perceptibly affected by hydrochloric acid, but is blackened by caustic soda or ammonia, showing that the mercuric salt is reduced to a mercurous compound.*

Copper sulphate ($CuSO_4$) in excess gives a green precipitate which on heating turns to a yellowish red, probably cuprous hydrate. If ammonia is added to the copper sulphate till the precipitate first formed is redissolved, then on adding sodium sulphite to the deep blue solution and boiling, the blue colour gradually becomes lighter, the cupric salt being reduced to the cuprous state. If caustic soda is now added, yellowish red cuprous hydrate is precipitated.

Many other compounds are reduced by sulphites, especially in acid solutions. Ferric salts are reduced to ferrous salts, chromates to salts of chromium, auric chloride to metallic gold, permanganates to manganese salts, &c.

Sulphurous acid is easily reduced to sulphuretted hydrogen, thus:—

$$SO_2 + 3H_2 = SH_2 + 2H_2O.$$
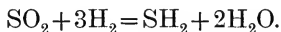
The smallest quantity of a sulphite (or sulphurous acid) introduced into a hydrogen generator (containing zinc and dilute sulphuric acid) is reduced, and sulphuretted hydrogen is evolved, which may be easily recognised by its producing a black stain on paper moistened with a solution of lead acetate. This reaction is analogous to the production of antimonuretted and arsenuretted hydrogen from salts containing antimony and arsenic. It should be noted, however, that arsenates give arsenuretted hydrogen, but sulphates do not give sulphuretted hydrogen.

Stannous chloride ($SnCl_2$) also reduces sulphurous acid to sulphuretted hydrogen, which precipitates the tin as sulphide. On adding an excess of stannous chloride to a solution of a sulphite acidified with hydrochloric acid, a white precipitate at first produced is redissolved, and a

yellow precipitate of stannic sulphide falls after long standing. The following equation probably expresses the change :—

$$2SO_2 + 8HCl + 6SnCl_2 = SnS_2 + 5SnCl_4 + 4H_2O.$$
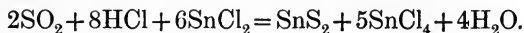
According to Fresenius the brown stannous sulphide (SnS) is produced, but the higher stannic sulphide appears to more generally result.

Sulphurous acid, or an acidified solution of a sulphite, gives a fine white precipitate of sulphur when *sulphuretted hydrogen* is passed into the solution. Some pentathionic acid and other compounds are also produced.

Thiosulphates

The normal thiosulphates have the general formula $M'_2S_2O_3$, in which M' stands for a monad metal.

The thiosulphates are often called " hyposulphites," the name they were at first known by. But as real hyposulphites have since been prepared, it is better to use the systematic name.

Thiosulphates are decomposed on ignition. Sodium thiosulphate gives sodium sulphate and tetrasulphide and sulphur:—

$$4Na_2S_2O_3 = Na_2SO_4 + Na_2S_4 + S.$$
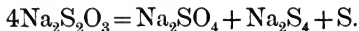
Use a solution of sodium thiosulphate ($Na_2S_2O_3,5H_2O$).

Hydrochloric acid and other dilute acids give a yellow precipitate of sulphur with evolution of sulphurous anhydride.* Potassium dichromate ($K_2Cr_2O_7$) does not liberate sulphurous anhydride.

Barium chloride ($BaCl_2$) gives no precipitate unless the solution is very strong.*

Silver nitrate ($AgNO_3$) gives a white precipitate of silver thiosulphate ($Ag_2S_2O_3$) which soon darkens to

yellow, brown, and finally black, because of its changing to sulphide,* thus :—

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$
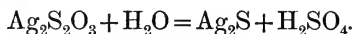
This change takes place especially on heating. The white precipitate is soluble in excess of sodium thiosulphate, and the solution when heated gives a precipitate of silver sulphide. But a considerable excess of the sodium salt confers comparative stability on the compound, and prolonged heating is necessary to effect the change. The changes produced here should be compared with those given by sodium sulphite.

Copper sulphate ($CuSO_4$) gives no precipitate at first with sodium thiosulphate; but by warming the solution a black precipitate of cuprous sulphide (Cu_2S) is obtained.* Excess of the sodium salt retards the reaction.

The soluble salts of many other metals, especially those of Group II, and even nickel and cobalt, give similar reactions to those of silver nitrate and copper sulphate just described.

Thiosulphates are oxidised to sulphates and free sulphuric acid by chlorine and compounds that yield it, such as sodium hypochlorite. Iodine oxidises sodium thiosulphate to the tetrathionate ($Na_2S_4O_6$).

Ferric chloride (Fe_2Cl_6) gives a violet colouration, which soon disappears especially on heating,* the ferric salt being reduced to ferrous, and the thiosulphate oxidised to sulphate.

Thiosulphates are reduced, and give sulphuretted hydrogen when introduced into a hydrogen generator. In this they resemble sulphites.

Sulphides

The normal sulphides have the general formula M'_2S, in which M' stands for a monad metal.

Sulphides are in many reactions analogous to the oxides.

Heated in a bulb tube, some give off sulphur. Gold sulphide gives off all its sulphur. Some of the higher sulphides of the heavy metals give off a part of their sulphur; iron pyrites (FeS_2) and stannic sulphide (SnS_2) are examples. The former is generally stated to give off one-third of its sulphur, leaving Fe_3S_4, but it appears to be a question of temperature whether or not it loses more than this. Ammonium sulphide is hardly known except in solution. Arsenious sulphide and mercuric sulphide sublime when heated, the first giving a yellow sublimate, and the other a steel-grey hard sublimate that turns to a bright red when finely ground. (Vermilion is mercuric sulphide properly prepared.) The other sulphides generally remain unaffected by heating them in the absence of air.

Heated in the presence of air, as in a sloping tube open at both ends, on platinum foil, or on charcoal in the outer blowpipe flame, sulphides are oxidised either to oxides or sulphates, with evolution of sulphurous anhydride.

The alkaline sulphides are soluble in water. The sulphides of the alkaline earths and magnesium are difficultly soluble, the rest are insoluble.

Hydrochloric acid and other dilute acids decompose the sulphides of the metals of Groups IV. and V., also of manganese, zinc and iron (but the mineral sulphides of iron are not attacked), with evolution of sulphuretted hydrogen (H_2S). Stronger hydrochloric acid attacks in a similar way the sulphides of antimony, tin and cadmium. The sulphuretted hydrogen evolved is easily recognised by its odour of rotten eggs, or by its blackening a piece of paper moistened with a solution of lead acetate or silver nitrate.* Other metallic salts obviously may be used for

testing, and the gas may be passed through the solution of a suitable reagent, instead of using a wetted paper.

Potassium dichromate does not give off sulphuretted hydrogen from sulphides.

Sulphuric acid, concentrated, must not be used to attack sulphides with, as sulphuretted hydrogen is evolved from it by many reducing agents, such as iodides, and metals like zinc and iron.

If the sulphide is in an aqueous solution, a solution of the metallic salt may be added at once to it. For this purpose a silver or cadmium salt is generally convenient, a black or a yellow sulphide being produced.*

Sulphides that are not attacked by hydrochloric acid can generally be easily identified indirectly. Being insoluble in hydrochloric acid, sometimes they can be obtained separate from other things that accompany them by dissolving every thing except the sulphide. The colour of the sulphide that remains, and the products of the action of nitric acid or aqua regia upon it, sometimes too its volatility, as in the case of mercury and arsenic sulphides, leave no room for doubt as to its identity. Nitric acid or aqua regia generally liberate sulphur; they always give a solution containing the metal unless the metal itself is changeable by them into an insoluble compound. Tin sulphide with nitric acid gives white insoluble metastannic acid. The sulphur is oxidised, at least partly, to sulphuric acid. Arsenious sulphide dissolved in aqua regia gives a solution that contains arsenic and sulphuric acids; ammonia and magnesium sulphate will precipitate the one, and barium chloride the other, after suitable dilution. Having proved that a certain metal and sulphur are present in an insoluble compound, the physical properties of the compound are generally sufficient to show what it is.

To discover and remove a sulphide that may be in a solution containing a sulphite and thiosulphate as well as a sulphate, precipitated cadmium carbonate is shaken up with the solution and filtered off. By adding acetic acid to the residue, a yellow insoluble remainder shows that a sulphide was present. The solution now contains a carbonate instead of a sulphide. If barium chloride is added, barium sulphate, sulphite and carbonate are precipitated, and the filtrate may be tested for thiosulphate. By treating the barium precipitate with dilute hydrochloric acid in the cold, the sulphite and carbonate dissolve the sulphate remaining, and the sulphite may be tested for by adding a little sodium hypochlorite to the solution, when it is oxidised to sulphate and precipitated. By this means these four acid radicals may be detected in the presence of each other.

Nitrates

The normal nitrates have the general formula $M'NO_3$, in which M' stands for a monad metal.

Nitrates when heated in a bulb tube generally fuse, though some do not; but they are always decomposed. Potassium and sodium nitrates give off oxygen with production of a nitrite;* at a higher temperature the nitrite is also decomposed, leaving an oxide or peroxide of the metal. Ammonium nitrate is decomposed into nitrous oxide (N_2O) and water, and the decomposition may be violent and accompanied by flame if it is heated quickly and vigorously. Generally some red fumes are evolved and a sublimate is produced. The nitrates of heavy metals give off red fumes of nitric peroxide (NO_2) and oxygen.

Heated on charcoal, nitrates cause deflagration, that is

the charcoal burns violently, throwing out sparks.* Some basic nitrates (as of bismuth) contain so little nitric acid, and what there is does not easily get into contact with the charcoal because it is so readily driven off by the heat, that deflagration may not ensue.

Hydrochloric acid when dilute does not decompose nitrates at a gentle heat. A more concentrated acid is oxidised by the liberated nitric acid, and chlorine and red nitrous fumes are given off:—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

The nitrosyl chloride is probably partially decomposed by the water present.

Sulphuric acid when concentrated causes the evolution of nitric acid, and, on warming, a part of the acid is often decomposed into the lower oxides of nitrogen, which show as reddish brown fumes. By adding a fragment of copper or similar metal, the nitric acid is more completely reduced and the red fumes are more copious.

A much more useful reaction than the last, though of the same character, consists in mixing the nitrate with strong sulphuric acid keeping the mixture cold, and then gently pouring on to the liquid a solution of ferrous sulphate, so that it does not mix but lies on the top as a distinct layer. The nitric acid liberated by the sulphuric acid as it comes into contact with the ferrous sulphate is reduced to nitric oxide, just as the copper reduces the acid in the previous case. But instead of warming the liquid and allowing the nitric oxide to escape into the air and produce red fumes, the liquid is kept cold, and the gas dissolves in the over-lying layer of ferrous sulphate producing the characteristic brown colour which a solution of nitric oxide in ferrous sulphate always has. This brown layer is often called a brown " ring "; but it is not a ring, it

is only a layer, and it is round only because the vessel used for the experiment is round. By heating, the nitric oxide is driven out from the solution and the colour disappears.*
The production of nitric oxide by the action of the ferrous sulphate upon the liberated nitric acid is shown by the following equation :—

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4$$
$$= 2NO + 3Fe_2(SO_4)_3 + 4H_2O$$
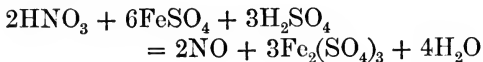
All normal nitrates are soluble in water, it is therefore impossible to test for nitrates by getting a precipitate by double decomposition, as is usual in most other cases. A few basic nitrates are not soluble in water.

Indigo dissolved in sulphuric acid is bleached or changed to a light yellow by nitric acid, or a mixture of sulphuric acid and a nitrate, on warming.* The indigo solution should not be added in greater quantity than sufficient to colour the liquid. This reaction does not distinguish nitric acid from other oxidising substances, such as chlorates and substances that evolve chlorine with sulphuric acid.

Brucine in small quantity dissolved in strong sulphuric acid gives a fine red colour when a solution of a nitrate is added to it.

Nitrates, if fused with sodium carbonate (or fusion mixture) form alkaline nitrates, and these are decomposed by the heat, leaving nitrites. The nitrite may be tested for as stated in the section on Nitrites, especially by the liberation of iodine from potassium iodide.*

Nitrates are reduced with the formation of ammonia by the action of several reducing agents, such as zinc foil coated with copper, a mixture of iron and zinc filings, or metallic aluminium. The reaction is best done in a solution containing excess of caustic alkali. By heating a

nitrate mixed with an organic substance, such as sugar, and an excess of an alkaline substance, such as lime, ammonia is evolved. Stannous chloride, when heated with an acidulated solution of a nitrate, produces an ammonium salt by reduction of the nitric acid. These reactions are of little use in general qualitative work.

Free nitric acid may be detected in the presence of nitrates by evaporating the solution with quill cuttings, white wool, or other similar white materials of animal origin. The animal matter is turned yellow by the free acid.

There is no ready way of qualitatively proving the presence of a nitrate when mixed with a nitrite.

Nitrites

The normal nitrites have the general formula $M'NO_2$, in which M' stands for a monad metal.

When heated in a bulb tube or on charcoal, nitrites resemble nitrates. Ammonium nitrite is hardly known in the solid form; its solution when warmed decomposes into nitrogen and water.

Sulphuric acid, dilute, when added to a nitrite, causes the liberation of nitric oxide (NO),* the nitrous anhydride oxidising a part of the nitrite to nitrate, itself being reduced to nitric oxide, thus:—

$$3KNO_2 + H_2SO_4 = 2NO + KNO_3 + K_2SO_4 + H_2O.$$
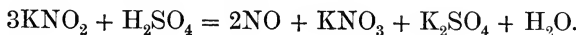
Most nitrites are soluble in water, and are therefore not generally detected by the formation of precipitates by double decomposition. The following two reactions may be noticed, though they are not of much use in proving the presence of nitrous acid.

Silver nitrate ($AgNO_3$) gives with solutions of alkaline

nitrites that are not too dilute a white precipitate of silver nitrite ($AgNO_2$), soluble in much water, more easily on warming.

Cobaltous salts in solution, with an excess of alkaline nitrite, followed by acetic acid in excess, give a yellow precipitate of potassium cobaltic nitrite. For further details of this reaction, see the section on Cobalt.

Ferrous sulphate behaves with nitrites as with nitrates. It is, however, not necessary to use strong sulphuric acid nor to keep the liquid in two layers. The ferrous sulphate solution should be added at once to the solution of the nitrite, and then a little dilute acid, and a dark brown colour, due to the solution of nitric oxide in the ferrous sulphate solution, immediately appears. The nitric oxide is driven off by heating.*

Sulphuretted hydrogen is oxidised by nitrites, especially in acid solutions, giving a copious precipitate of sulphur.*

Potassium iodide is also oxidised with liberation of iodine on adding it to a solution containing a nitrite, and then acidifying. To detect a small quantity of nitrous acid, starch paste should be introduced with the iodide. A minute amount of a nitrite is then shown on acidification by the production of the blue iodide of starch.*

Potassium permanganate solution is decolourised, after acidification, by a nitrite, the nitrite being oxidised to nitrate.

Auric chloride also oxidises nitrites with precipitation of metallic gold.

Chlorates

The normal chlorates have the general formula $M'ClO_3$, in which M' stands for a monad metal.

Chlorates are in many respects analogous to nitrates, and give similar reactions. The possibility of reducing a chlorate to a chloride is a quite distinctive change.

Chlorates are decomposed when heated in a bulb tube with evolution of oxygen, which is mixed with chlorine if the basic radical is a metal which retains oxygen more tenaciously than chlorine. The alkaline chlorates fuse and give off oxygen which is nearly pure, leaving the chloride of the metal.*

Heated on charcoal, chlorates cause deflagration even more readily than nitrates.* Other oxidisable substances, such as sulphur and sulphides, powdered metals, and organic matter in general, are so readily attacked by chlorates that it is not safe to mix them together. Violent detonations may be produced by rubbing them together, as in a mortar.

Hydrochloric acid when dilute has no action on chlorates unless the mixture is warmed. Stronger hydrochloric acid on heating decomposes the chlorate with evolution of a mixture of chlorine peroxide and chlorine,* thus :—

$$4KClO_3 + 12HCl = 3ClO_2 + 9Cl + 4KCl + 6H_2O.$$
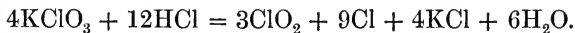
This mixture of gases is of a very much deeper yellow colour than chlorine alone, and it is not dangerously explosive as the peroxide of chlorine is by itself.

Sulphuric acid, strong, causes the liberation of chlorine peroxide, and as this gas is decomposed with violent detonation when slightly heated, very small quantities of the chlorate should be used. Chlorine peroxide is a heavy yellowish red gas. In using this reaction for the detection of chlorates, it is safer to gently warm a little strong sulphuric acid in a test tube, and then to drop into the acid a very small fragment of the substance to be tested. A few sharp cracks or small detonations will take place if a chlorate is present.*

The production of the chlorine peroxide from the chlorate is analogous to the production of nitric oxide

from nitrites when they are acted on by acids. One part of the chlorate gives up oxygen to another, the first being reduced to chlorine peroxide, and the second oxidised to a perchlorate, thus :—

$$3KClO_3 + 2H_2SO_4$$
$$= 2ClO_2 + KClO_4 + 2KHSO_4 + H_2O.$$
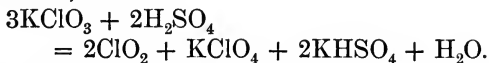
All chlorates are soluble in water; like nitrates and nitrites, therefore, they cannot be detected by the usual methods of double decomposition.

Indigo dissolved in sulphuric acid is bleached to a yellow colour by chlorates as by nitrates, on heating. The indigo is changed even in the cold if a little of a sulphite or a drop or two of sulphurous acid solution is added to it in addition to the chlorate. The exact action of the sulphite is not very clear, but probably it reduces the chlorate to a less stable compound. The indigo should be sparingly used in these tests.*

If a chlorate and a nitrate are together, the substance should be mixed with fusion mixture, unless only alkaline salts are present, and fused on platinum until the effervescence due to the escape of oxygen has nearly ceased. The residue is dissolved in water, and tested for chlorides with nitric acid and silver nitrate, and for nitrites with either ferrous sulphate and hydrochloric acid, or with potassium iodide and starch and a dilute acid. By the ignition the chlorate and nitrate are decomposed, leaving a chloride and a nitrite respectively. If a chloride is present from the first, it must be got rid of by precipitating it from the solution with silver sulphate. The filtrate is then evaporated, mixed with fusion mixture, dried, and fused. If a nitrite is originally present, it interferes with the detection of the nitrate, because there is no ready means of qualitatively finding a nitrate in the presence of a nitrite.

Hypochlorites

Hypochlorites when heated are decomposed into chlorates and chlorides, and the chlorates undergo further decomposition. The decomposition of hypochlorites may be effected even by heating them in solution.

Bleaching powder, the so-called " chloride of lime," is the commonest example of a hypochlorite. It is prepared by causing slaked lime to absorb chlorine, and is a compound of the hypochlorite, chloride, and hydrate of calcium. The hypochlorite and chloride are present molecule for molecule, but the proportions of the hydrate and water probably vary, for opinions differ respecting them.

The so-called " chloride of soda " or " sodium hypochlorite " is also a compound or mixture in solution of an equal number of molecules of sodium chloride and sodium hypochlorite.

These preparations are sometimes called chloro-hypochlorites, and formulated as double salts. Thus bleaching powder, excluding the calcium hydrate and water (which, however, appear to be essential for its existence), may be written $Ca(OCl)Cl$ instead of $Ca(OCl)_2 + CaCl_2$.

Dilute acids, even carbonic acid, liberate chlorine, thus :—

$$NaOCl + NaCl + 2H_2SO_4 = Cl_2 + 2NaHSO_4 + 2H_2O.$$
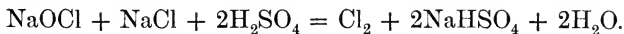
The chlorine may be recognised in several ways, but the best is by its power to bleach litmus. The solution to be tested should have a little litmus extract added to it, and then a drop or two of a dilute acid.* If the hypochlorite is in sufficient quantity its solution may be acidified and warmed, and the liberated gas allowed to act on moistened litmus paper. But this is not so characteristic a method as the other.

Indigo is readily bleached to a yellow colour by chlorine, and therefore by an acidified solution of an hypochlorite.*

Hypochlorites oxidise many metallic compounds, and several examples of this effect have been already given. The black nickelic, cobaltic and manganic hydrates, and the brown lead dioxide may be produced by its means. The oxidation of chromium salts to chromates has been described in the section on Chromium.

Chlorides

The normal chlorides have the general formula $M'Cl$, in which M' stands for a monad metal.

Chlorides vary in their behaviour when heated in a bulb tube. Ammonium chloride and the chlorides of mercury easily volatilise, giving white sublimates.

Mercuric chloride fuses, ammonium and mercurous chloride do not. Silver chloride fuses easily; lead chloride also fuses; potassium and sodium chlorides require a higher temperature, but they also fuse when heated in glass tubes. Other chlorides that are not so often met with in an anhydrous condition, such as those of iron, manganese and copper, are also fusible. Stannic chloride and the pentachloride of antimony are liquids that may be distilled. The chlorides of gold and platinum are decomposed on ignition into the metal and chlorine. Anhydrous ferric chloride, when heated out of contact with air, is easily volatile, but in the hydrated condition in which it is usually met with, the oxide of the metal remains and hydrochloric acid escapes. Even the anhydrous ferric chloride heated in contact with air is decomposed, yielding oxide and free chlorine. Moist magnesium chloride when heated loses hydrochloric acid and leaves the oxide or oxychloride; and other chlorides show the same tendency

to suffer decomposition when heated in a moist state, or when their solutions are evaporated.

At higher temperatures almost all chlorides are volatile unless they are decomposed by the heating. Silver chloride is volatile even when heated in a porcelain crucible over a blowpipe, so also are potassium and sodium chlorides. The volatility of chlorides as a class is taken advantage of in getting characteristic flame colourations which serve for the detection of various metals.

If a microcosmic salt bead is strongly coloured with oxide of copper and heating in the outer blowpipe flame, and then a small quantity of a substance containing chlorine is added to it and the bead is heated in the inner flame, the chloride of copper produced volatilises and imparts a fine blue colour to the outer flame.*

Hydrochloric acid, dilute, for obvious reasons does not cause the evolution of any gas when added to chlorides.

Sulphuric acid, concentrated, acts upon most chlorides, causing the evolution of hydrochloric acid, which fumes in the air and strongly reddens blue litmus paper.* The chlorides of the alkalies and ammonium are acted on even in the cold with much effervescence. But the chlorides of silver, lead, mercury and tin are not attacked. If sulphate of lead is dissolved in hydrochloric acid, it is the chloride and not the sulphate of lead that separates on cooling.

Oxidising substances, such as manganese dioxide, if present with the chloride and sulphuric acid, oxidise the hydrochloric acid, and chlorine is evolved instead. The chlorine is distinguished especially by its power to bleach moistened litmus paper.* Nitrates have a similar action, but the chlorine is then accompanied by red nitrous fumes.

Dry potassium dichromate, mixed with a dry chloride, yields, when warmed with strong sulphuric acid, red

fumes which condense to a red liquid, of chromyl chloride (CrO_2Cl_2),* also called chlorochromic acid or chlorochromic anhydride. A few drops of the liquid can easily be distilled over :—

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4$$
$$= 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O.$$
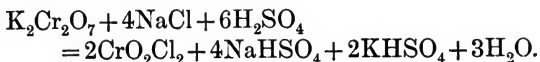
This reaction sometimes forms an important test for chlorides, because neither bromides nor iodides produce analogous compounds. The essential feature of the reaction is that chromium has been rendered volatile, and that under such conditions chromium cannot be volatilised except in combination with chlorine, therefore if chromium is in the distillate, chlorine must have been present. To test for the chromium, add water to the distillate, when chromic and hydrochloric acids are produced, thus :—

$$CrO_2Cl_2 + 2H_2O = 2HCl + H_2CrO_4.$$
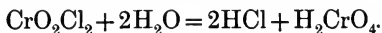
The solution may be tested by adding ammonia to it, when it remains yellow, or by adding lead acetate, when a yellow precipitate of lead chromate falls. Bromine which is produced from bromides by the same reagents, and has a very similar appearance to chromyl chloride, gives a colourless solution with ammonia, and of course no chromate of lead with the lead salt.

Chlorides generally are soluble in water, except silver and mercurous chlorides. Lead chloride is sparingly soluble in cold water, but readily in hot. A few basic chlorides are insoluble or sparingly soluble, especially those of bismuth and antimony ; but these dissolve easily in hydrochloric acid. Cuprous chloride is insoluble in water, but soluble in hydrochloric acid.

Silver nitrate ($AgNO_3$) added to a solution of a chloride gives a white curdy precipitate of silver chloride ($AgCl$).

The precipitate is insoluble in nitric acid; it is therefore best to add dilute nitric acid before the silver salt, to prevent the precipitation of other silver compounds which might be formed in a neutral solution. It is readily soluble in ammonia, and reprecipitated on acidification of the solution, unless there is a very small quantity of it.* It is soluble in strong solutions of alkaline chlorides, especially ammonium chloride, and partially reprecipitated by diluting. It is readily soluble in solutions of potassium cyanide or sodium thiosulphate, and soluble, but not so easily, in a solution of sodium sulphite. By exposure to light silver chloride darkens in colour, losing a little of its chlorine.

Insoluble (and other) chlorides are decomposed by fusion with fusion mixture with formation of alkaline chlorides; but this operation is rarely necessary, because the chlorides not soluble in dilute hydrochloric acid are easily identified. Silver chloride is soluble in ammonia, darkens on exposure to light, and is fusible to a horny mass. Mercurous chloride is easily soluble to mercuric chloride by the action of chlorine (sodium hypochlorite), and it is blackened by alkalies. Lead chloride is soluble in hot water, and the solution gives a yellow precipitate with potassium chromate.

Free hydrochloric acid, unless in considerable quantity, is not very easily detected in the presence of the chlorides of the heavy metals which themselves have an acid reaction to litmus. Perhaps the best method is to heat the solution with manganese peroxide and test for the chlorine evolved. Evidently the whole of the chlorine of the free acid cannot be given off:—

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O.$$
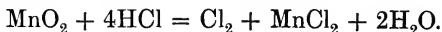
Bromides

The normal bromides have the general formula M'Br, in which M' stands for a monad metal.

Bromides are affected by ignition very much like chlorides, but the tendency to lose the halogen is rather greater.

On a bead of microcosmic salt containing copper oxide, bromides colour the flame very much as chlorides do, but the colour is rather greener towards the edges.

Hydrochloric acid when dilute does not perceptibly affect bromides.

Sulphuric acid, strong, when warmed with a bromide, gives rise to the evolution of hydrobromic acid, a part of which reacts with the sulphuric acid and forms free bromine and sulphurous anhydride,* thus :—

$$2HBr + H_2SO_4 = SO_2 + Br_2 + 2H_2O.$$
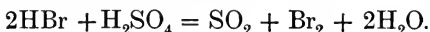
Sulphuric acid, with manganese dioxide, potassium dichromate, a nitrate, or other similar oxidiser, gives off bromine as a reddish brown vapour that condenses to a dark liquid.* The distinction between bromine and chromyl chloride is given in the section on Chlorides.

In solubility the bromides are very analogous to the corresponding chlorides.

Silver nitrate ($AgNO_3$), added to a solution of a bromide, gives a yellowish white precipitate of silver bromide ($AgBr$). The precipitate is insoluble in nitric acid, difficultly soluble in ammonia and reprecipitated on acidification,* more readily soluble in sodium thiosulphate, and quite easily soluble in potassium cyanide. The precipitate darkens to a violet colour by exposure to light, but is not so much affected in colour as silver chloride under similar circumstances.

Chlorine liberates bromine from bromides. Chlorine water may be added to the solution, or hydrochloric acid may be first added, and then a drop of sodium hypochlorite. The liberated bromine, if in sufficient quantity, imparts its characteristic reddish colour to the solution; but it is better to add a drop or two of bisulphide of carbon or chloroform and shake up, when, on allowing it to stand, the bisulphide or chloroform settles to the bottom, and shows clearly the red colour of the bromine dissolved in it.* Ether or benzene may be used, for they act similarly in dissolving the bromine out from the liquid, but, being lighter, they float on it. This is the test that is most generally relied on for proving the presence of a bromide.

Starch is coloured yellow by free bromine.

The detection of a bromide is not interfered with by the presence of a chloride. To detect a chloride in the presence of a bromide, it may be noted that on adding silver nitrate to the mixed solution silver bromide is precipitated before the chloride. By a partial precipitation, filtering and adding more silver nitrate, the chloride may sometimes be detected; but this method is of little use. Silver chloride is distinguished from silver bromide by its much more ready solubility in ammonia and by its white colour.

If silver bromide and chloride are precipitated together, the chloride may be identified by adding water to the precipitate, then two or three drops of the ordinary dilute ammonia, shaking up and filtering. Such diluted ammonia will not dissolve a discoverable amount of the bromide, but on acidification with nitric acid a very notable amount of silver chloride will be precipitated if a chloride was originally present. The reprecipitated chloride is white, and will redissolve at once on adding ammonia. It

should be noticed that an excess of silver nitrate must be added in getting the first precipitate, as the bromide comes down first.

Bromine may be got rid of from a solution that contains both a chloride and a bromide by adding a good excess of dilute sulphuric acid, boiling the liquid in a dish, and adding, a drop at a time, a solution of potassium permanganate to the boiling liquid, until a drop of the permanganate imparts a pink tint to the liquid. The boiling should be continued for a few seconds, to drive out the remainder of the liberated bromine. The solution is then cooled and tested with silver nitrate as usual for the chloride. This method will not serve to detect a trace of a chloride in the presence of the bromide, as a little chlorine is driven out, unless indeed a little bromine is allowed to remain, which of course would vitiate the test in any case. The permanganate will decompose both the chloride and the bromide; but so long as any unattacked bromide remains, the permanganate is decolourised as soon as it is added, and so does not give a permanent tint to the solution.

The production of chromyl chloride, as described in the section on Chlorides, may be utilised for finding a chloride in the presence of a bromide; but the test is not so easily performed as the others here given.

Iodides

The normal iodides have the general formula $M'I$, in which M' stands for a monad metal.

The tendency to lose the halogen on ignition is even greater with iodides than bromides, so that most iodides are decomposed by heating them. The iodides of potassium and sodium fuse without decomposition.

On a microcosmic salt bead to which copper oxide has been added, iodides impart an intense emerald green colour to the flame.

Hydrochloric acid, dilute and cold, does not perceptibly affect iodides. Nor does it on gentle warming; but, if boiled, decomposition may ensue with liberation of the violet vapour of iodine.

Sulphuric acid, strong, when warmed with an iodide, liberates a very little or no hydriodic acid, for the acid set free is oxidised by the sulphuric acid with the production of iodine, sulphurous anhydride and sulphuretted hydrogen; and the two latter gases, by reacting together, set free sulphur.* The production of sulphurous anhydride and sulphuretted hydrogen by the action of the hydriodic acid or the sulphuric acid, is shown in the following equations :—

$$H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O$$
$$H_2SO_4 + 8HI = H_2S + 4I_2 + 4H_2O.$$
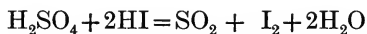
Sulphuric acid with oxidisers, such as manganese dioxide, potassium dichromate, &c., gives off iodine from iodides, which appears as a violet vapour, and condenses to a steel-coloured solid sublimate.*

Silver, mercurous, cuprous and lead iodides are as to solubility analogous to the corresponding chlorides. Lead iodide crystallises from its solution in hot water in beautiful yellow crystals. Mercuric and bismuth iodides are also insoluble, though their chlorides are soluble.

Silver nitrate ($AgNO_3$) gives with solutions of iodides a yellowish white precipitate of silver iodide (AgI) which is insoluble in nitric acid, practically insoluble in ammonia,* soluble in potassium cyanide or sodium thiosulphate. The precipitate darkens on exposure to light.

Mercuric chloride ($HgCl_2$) gives a fine vermilion-coloured

precipitate of mercuric iodide (HgI_2), which dissolves in excess of either the iodide or the mercury salt.*

Cupric sulphate ($CuSO_4$) gives a whitish precipitate of cuprous iodide (Cu_2I_2), an equivalent amount of iodine being liberated. If ferrous sulphate or sulphurous acid is also added, the whole of the iodine is precipitated as cuprous iodide,* thus :—

$$2CuSO_4 + 2KI + H_2SO_3 + H_2O$$
$$= Cu_2I_2 + K_2SO_4 + 2H_2SO_4.$$
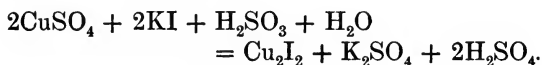
Neither bromides nor chlorides give a precipitate in this manner.

Chlorine, bromine, nitrous acid (or nitrites), and many other oxidising agents such as cupric or ferric salts, added to neutral or acid (with nitrites the acid is necessary) solutions of iodides, liberate iodine.* If much iodine is set free it will form a steel-grey scaly precipitate; moderate quantities give a reddish solution.

Starch paste diluted with much water gives a deep blue colour with the liberated iodine. The starch may be added before the iodine is liberated, and the blue colour then appears as soon as it is set free.* This reaction is exceeding sensitive and characteristic, and should never be omitted when it is sought to prove the presence of iodine or an iodide. The blue colour of the so-called "iodide of starch" disappears on warming, or by the addition of substances that will combine with the iodine, such as alkalies, sulphuretted hydrogen (which forms hydriodic acid and sulphur), sulphurous acid, or even excess of chlorine (forming chloride of iodine). This action of excess of chlorine renders chlorine water or sodium hypochlorite not so suitable for use in the detection of small quantities of iodine as nitrous acid or nitrites in the presence of an acid.

Chloroform, bisulphide of carbon, ether or benzene, preferably one of the two first, may be agitated with the solution containing the liberated iodine. The iodine is concentrated in the few drops of the solvent that settle to the bottom (or with ether or benzene rise to the surface), colouring it a reddish violet.* The colour in ether, however, is reddish brown, and similar to the colour produced by bromine. If both iodides and bromides are present, the iodides not in too small a quantity, chloroform or carbon disulphide may be added to the liquid to be tested, and then chlorine water—a very little at a time—with agitation after each addition. The colour due to iodine then appears first, and with excess of chlorine this is removed and the colour due to bromine appears in the drop or two of heavy liquid at the bottom.

The detection of an iodide in the presence of chlorides and bromides offers no difficulty. The iodine may then be removed as cuprous iodide with cupric sulphate and sulphurous acid, the sulphurous acid boiled off from the filtrate, then the bromide and chloride may be detected as described in the section on Bromides.

Fluorides

The normal fluorides have the general formula $M'F$, in which M' stands for a monad metal.

Although fluorine is so intimately related to the other halogens, chlorine, bromine, and iodine, for practical analytical purposes, fluorides have very little resemblance to chlorides, bromides, and iodides. Calcium chloride is exceedingly soluble in water and very deliquescent; calcium fluoride, the well-known fluor-spar, is insoluble in water. Silver chloride is insoluble, but silver fluoride is soluble in water. The liberation of hydrofluoric acid

from fluorides by the action of sulphuric acid is analogous to the liberation of hydrochloric acid by the same means, but this is the only analogy that exists between the two classes of salts, so far as their properties are utilised in analytical work.

Fluorides are not generally altered by ignition, except that some of the rarer ones are volatile, and some, including the alkaline fluorides, are fusible.   But many fluorides if heated in a moist state give off a little hydrofluoric acid with the moisture, and this settling on the cooler part of the tube corrodes the glass, producing a roughening and a small deposit of silica that looks like a sublimate formed by volatile matter.   Heating the deposit fails to drive it away, and proves that it is not volatile.

Hydrofluoric acid in quantity may be liberated by mixing a fluoride with hydrogen potassium sulphate or microcosmic salt, and heating the mixture. These methods are not desirable unless the analyst has restricted accommodation, as when blowpipe apparatus only is desirable.

Sulphuric acid, strong, attacks fluorides, (except some minerals of a complex character) and hydrofluoric acid is evolved on warming ; the reaction takes place with some even in the cold.   Hydrofluoric acid is a fuming acid gas, even more irritating and dangerous to inhale than hydrochloric acid.   It is distinguished from all other acids by its power to attack silica and form with it the volatile gas, silicon fluoride (SiF_4).   This distinctive property of the acid is invariably utilised in proving the presence of a fluoride.   The reaction is applied in two methods.

If the fluoride is not mixed with silica or a borate (for boric acid is acted on like silicic acid), the fluoride, or substance to be tested, is put into a small leaden cup or

platinum capsule, mixed with a little strong sulphuric acid, and a watch glass that has its convex surface partly protected by wax and partly exposed is placed convex side downwards as a cover to the capsule. The arrangement may then be left for several minutes, and if the action of the sulphuric acid is very sluggish, the capsule may be very gently warmed. After the action, the watch glass is warmed and the wax wiped off, and search is made for the corrosion of the surface where the glass was exposed. The corrosion will show as cuts or depressed parts if considerable, or a mere roughening of the surface if slight. If very slight, breathing gently on the thoroughly cleaned glass may show where the surface has been affected. To coat the glass, it should be cleaned, then warmed and the wax rubbed over it, and it may be warmed again to get an even coating. The wax should be removed in fine lines by a pointed instrument that will not scratch the glass, a pointed piece of hard wood such as is used for pensticks is as good as anything for the purpose.*

If the fluoride is in the immediate presence of silica or a silicate, then the hydrofluoric acid expends its energy on the silica, and silicon fluoride is evolved which does not attack glass, thus :—

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$
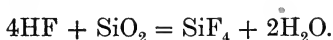
The silicon fluoride is a fuming irritating gas. The value of it to the analyst is due to its containing silicon, and silicon is not rendered volatile under any conditions similar to those stated, except in combination with fluorine. If, therefore silicon is proved present in the gas evolved, fluorine must have been present in the substance. This operation may be done in a test tube. If an appreciable quantity of silicon fluoride is evolved, a glass rod on which a drop of

water hangs may be lowered into the vertical tube carefully, so as not to touch the sides, and the drop of water will become encrusted over with silicic acid, so that it will appear to have been solidified. If the drop is crushed on a piece of litmus paper, the water will be found strongly acid from the hydrofluosilicic acid formed.* The change is thus represented :—

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2(2HF,SiF_4).$$

If the amount of silicon fluoride is too small to be rendered evident in this way, it may be swept over by a current of carbonic anhydride into a dilute solution of ammonia. Ammonium fluoride and hydrated silica will be produced (as ammonia decomposes hydrofluosilicic acid), and by evaporating the clear solution the fluoride may be obtained, or it may be precipitated with calcium chloride and the precipitate further examined.

The fluoride may, however, be separated from the silica and examined by the etching test, and this method is useful for detecting fluorides in combination with silica in minerals that are not attacked by sulphuric acid. Such minerals are fused with fusion mixture, the mass is extracted with water, and to the solution which contains the silica and hydrofluoric acid as alkaline salts, hydrochloric acid is added till it is acid, and then, to precipitate the silica, ammonia is added and the mixture is kept warm for a short time. Calcium chloride is then added to the filtrate, and the precipitated calcium fluoride is filtered off and examined as described above. The getting of a precipitate with calcium chloride is no proof of the presence of a fluoride unless the precipitate is proved to show the characteristic reactions of fluorides.

The fluorides of the alkalies, mercury, silver and aluminium, and stannous and ferric fluorides, are soluble in

water; while the fluorides of the alkaline earths, copper, lead, and zinc are practically insoluble.

Calcium chloride ($CaCl_2$) added to a solution of a fluoride gives a transparent gelatinous precipitate of calcium fluoride (CaF_2), which becomes more noticeable by the addition of ammonia.* The precipitate is dissolved on heating it with hydrochloric acid, and being soluble in ammonium salts may not be reprecipitated on adding ammonia. Acetic acid does not prevent the precipitation. This reaction is sometimes of use for separating fluorine from other substances that interfere with its detection, but must not be accepted as proof of the presence of a fluoride until the precipitate has been examined by one or other of the characteristic methods given above.

Calcium fluoride is partially decomposed by fusion with fusion mixture, but completely decomposed, with formation of alkaline fluorides, only in the presence of silica.

Silicofluorides

The normal silicofluorides have the general formula $2M'F,SiF_4$, in which M' stands for a monad metal.

The silicofluorides when heated are decomposed into silicon fluoride, which is evolved, and the fluoride of the metal.

The free acid when evaporated is similarly decomposed into hydrofluoric acid and silicon fluoride, it should not therefore be heated in glass vessels.

Silicofluorides are decomposed by warming them with strong sulphuric acid, and the evolved hydrofluoric acid will attack glass.

Barium and potassium salts give precipitates when they are added to hydrofluosilicic acid, as is stated in the sections dealing with those metals.

Ammonia decomposes the acid with the formation of ammonium fluoride and separation of hydrated silica.

Silicates

The anhydride has the formula SiO_2.

Silicates are not changed when heated in a bulb tube, unless they are hydrated and give off water.

Heated on charcoal some fuse and some do not.

Heated on a bead made of sodium carbonate, silicates cause effervescence, and in some cases give a transparent bead which remains transparent on cooling. To get this result a sufficiency of the silicate must be employed.

Heated on a bead made from microcosmic salt, a fragment of a silicate is changed into a " silica skeleton "; the bases are dissolved out, leaving a spongy residue of the same shape as the original fragment. It is obvious that the bases present may colour the bead.

Silicic acid is not volatile from solutions on heating.

Potassium and sodium silicates are soluble in water, though with great difficulty if they are free from excess of alkali. Alkaline silicates are formed when silicates are fused with fusion mixture. A little sand may be fused well with about six times its bulk of fusion mixture on platinum foil, the residue boiled in water and filtered if necessary, and with the solution the following tests may be made.*

Ammonium chloride (AmCl) or *carbonate* (Am_2CO_3), gives in solutions of alkaline silicates, a gelatinous precipitate of hydrated silica (H_4SiO_4),* thus :—

$$Na_4SiO_4 + 4AmCl = H_4SiO_4 + 4NaCl + 4NH_3.$$

Dilute acids decompose alkaline silicates precipitating hydrated silica, but the separation of the silica is not com-

plete, and in dilute solutions or with excess of acid it may remain entirely in solution. Even in this case the silica is liberated from the bases it was combined with, and it can be made quite insoluble by dehydrating it. By evaporating the solution to dryness, and continuing the heating, preferably on a water bath, until no more acid fumes are evolved, the silica is made anhydrous, and by moistening the residue with hydrochloric acid and warming it with water, the chlorides of the metals are dissolved and a white residue of silica is obtained.* The hydrochloric acid added to the residue is unnecessary if only alkalies are present, but with other metals it is desirable to ensure their complete solution. This method makes certain of the separation and detection of the smallest quantity of silica, and is the one that should be used whenever possible.

Some silicates, although insoluble in water, are decomposed by hydrochloric acid, the silica separating partly in the gelatinous form. They are best treated with the acid, and the mass evaporated to dryness and extracted with hydrochloric acid and water, as described above. The metals are thus obtained as chlorides separate from the silica, and their detection offers no difficulty.

Strong or slightly diluted sulphuric acid when hot will attack some silicates that hydrochloric acid fails to affect; but for the purpose of qualitative analysis, unless the nature of the silicate is already known, this method is rarely worth trying.

All silicates may be decomposed by fusion with fusion mixture. The substance should be finely ground and mixed with about six times its bulk of fusion mixture, and heated in a platinum capsule or on platinum foil until the melted mass is quiet and the action appears complete. It is then put into a porcelain dish with water, and hydrochloric acid is added at once. The contents of the dish

are warmed until the mass is completely disintegrated and the carbonates are decomposed, and then evaporated to dryness, and extracted with hydrochloric acid and water as already described.

Hydrofluoric acid (HF) attacks all silicates forming silicon fluoride (SiF_4) which passes off, leaving the metals as fluorides. It is preferable to add sulphuric acid as well, then the metals remain as sulphates and all the hydrofluoric acid is available for attacking the silica. This operation is done in a platinum vessel, and ample allowance made for the escape of the noxious fumes into the open air. The silicate may be mixed with calcium fluoride, and the mixture treated with strong sulphuric acid. In this case calcium sulphate remains with the sulphates of the other metals. , Hydrofluoric acid is chiefly of use for getting at the alkalies in silicates, as obviously they cannot be detected after fusion with alkaline carbonates.

The alkalies in silicates may be separated by heating the finely powdered material with barium hydrate, treating with acid, evaporating, and so on, to separate the silica as already described. But the most convenient method of all is to grind the material with an equal weight of ammonium chloride, then to mix this intimately with about ten times as much by weight of precipitated calcium carbonate as of the substance taken, and to heat the mixture gently at first, until the ammonia is driven off, then strongly for from half-an-hour to an hour. A platinum crucible should be used. The ammonium chloride is introduced for the purpose of getting a little calcium chloride in the mixture, and the calcium chloride performs the double function of causing a slight fusion or sintering of the mass, and of providing chlorine for the alkalies. By adding water to the cooled mass, the lime slakes and

the whole of the alkalies with some calcium dissolve as chlorides, with calcium hydrate. Ammonium carbonate will precipitate the calcium, and the filtered solution is evaporated to dryness and the alkalies detected as usual.

The amorphous silica that is separated as described above, may be tested as to its purity by boiling it with a solution of potassium or sodium hydrate or carbonate, when it will dissolve.

Borates

The anhydride has the formula B_2O_3.

Most borates fuse when heated to a moderate temperature. Those which contain water generally swell up as they give off their water.

The borates of the alkalies are soluble in water forming alkaline solutions; most other borates are difficultly soluble in water, but soluble in the presence of ammonium chloride or in dilute acids.

Borax ($Na_2B_4O_7,10H_2O$) may be used for the following tests.

Acids added to a strong solution of borax in the cold give a crystalline precipitate of boric acid (H_3BO_3) which is only slightly soluble in cold water.* Boric acid is more soluble in alcohol than in water.

An aqueous solution of free boric acid cannot be evaporated without loss of acid.

Barium chloride ($BaCl_2$), *calcium chloride* ($CaCl_2$), *silver nitrate* ($AgNO_3$), and other salts give precipitates of the borates of the metals in aqueous solutions of borax that are not too dilute.* These reactions are not distinctive and are of no use for the identification of boric acid.

Borates, if made into a paste with *sulphuric acid*, or if ground with hydrogen potassium sulphate and moistened with water, and then brought on a loop of platinum wire

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near to but hardly touching the lower part of the flame of a Bunsen burner, impart a green tinge to the flame where the vapour of the volatilised boric acid passes into it.*

If calcium fluoride is added to the paste made with sulphuric acid and the borate to be tested, the green colour imparted to the flame is much more striking ; and by this means small proportions of boric acid that would otherwise escape detection may be easily found.*   In this reaction it is the gaseous boric fluoride (BF_3) that is formed and colours the flame.

Instead of using the flame of a burner, the paste of sulphuric acid and the borate may be mixed with excess of alcohol in a small dish, and the alcohol lighted.   The flame will be coloured green, especially at the edges, and by stirring up the liquid with a glass rod the colour will be made more intense.*

Of these three methods of detecting borates by means of the green colour that liberated boric acid produces in the flame, the second is much to be preferred as being the most sensitive and the least liable to be interfered with by other substances.   Barium salts do not affect these tests, as barium sulphate is not volatile under the given conditions.   Of other substances that give a green colour to the flame, copper salts, chlorides in general, and phosphates must be considered.   Copper salts affect all the methods, but the second less than the other two, because boron fluoride is so easily volatile.   In either the first or the second, especially the second, if the borate is present in fair quantity, it can easily be distinguished in the presence of copper after a little practice.   The boric acid or boric fluoride give their colour to the flame before the pasty mass on the wire is brought into actual contact with the flame, indeed as soon as the mass begins to fume, it may be an eighth of an inch from the visible boundary

of the flame. If copper gives any colouration at this stage, it is generally due to the spluttering of the mass and the projection of particles into the flame. To make sure of the presence of a little boric acid in the presence of copper, the copper should be removed from the substance, generally by sulphuretted hydrogen, and the solution evaporated, keeping it alkaline with sodium hydrate or carbonate, and the residue tested by the second method. Hydrochloric acid, if present when alcohol is used, may produce a little ethyl chloride (C_2H_5Cl), and this burns with a green-edged flame. Phosphoric acid gives a whitish-green flame, and a phosphate mixed with sulphuric acid will produce the colour, but it is, like the colour produced by copper salts, not likely to show until the pasty mass is brought quite into the flame, and it is often hardly noticeable even then. In searching for small quantities or traces of boric acid, all these interfering substances should be absent.

Turmeric paper is changed to a brownish-red colour if dipped into a solution of boric acid and dried in a water oven or on a flask containing hot water. A solution of a borate to be examined by this method should be slightly acidified with hydrochloric acid, the turmeric paper dipped partly into it and dried.* If too much hydrochloric acid is present, in the absence of boric acid, the turmeric paper is coloured to a blackish-brown tint; but the colour due to boric acid is tolerably distinct. It is important that the solution should be acid to litmus, as alkalies change the yellow colour of turmeric to reddish-brown.

Phosphates

The normal ortho-phosphates have the general formula M'_3PO_4, in which M' stands for a monad metal.

When heated in bulb tubes, phosphates give no characteristic indication of the acid.

A dry phosphate heated with dry sodium carbonate and metallic magnesium or sodium in a narrow tube, so that air may be excluded, is reduced and gives an alkaline phosphide; and when the mass is moistened with water it gives off phosphoretted hydrogen, recognisable by its odour, resembling that of rotten fish.

Phosphates in which the hydrogen of the acid is only partially replaced or is replaced by ammonium, lose water or water and ammonia on ignition, and leave pyro- or metaphosphates. Thus, hydrogen disodium phosphate gives sodium pyrophosphate :—

$$2HNa_2PO_4 = Na_4P_2O_7 + H_2O.$$
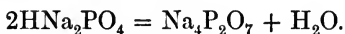
Microcosmic salt gives sodium metaphosphate :—

$$HNa(NH_4)PO_4 = NaPO_3 + NH_3 + H_2O.$$

Magnesium ammonium phosphate gives magnesium pyrophosphate :—

$$2(NH_4)MgPO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$
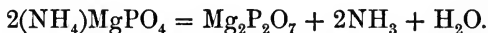
Pyro- and meta-phosphates give different reactions from the ordinary or ortho-phosphates, for general analytical purposes therefore they are converted into orthophosphates. By boiling with strong acids (hydrochloric or nitric), or, better, by fusion with fusion mixture, pyro- and meta-phosphates are converted into ortho-phosphates.

Phosphates of the alkaline earths, and of aluminium and chromium, are not decomposed by alkalies in aqueous solution, nor even by fusion with fusion mixture, unless silica is also present. They are, however, readily decomposed by other methods.

Acids, either dilute or strong, produce no change on phosphates that is characteristic of the acid.

The phosphates of the alkalies are soluble in water, and their solutions react alkaline towards litmus paper; almost all others are insoluble in water, but soluble in acids. It follows therefore that almost any soluble metallic salt will give a precipitate when added to the solution of an alkaline phosphate. A few only are practically useful for analytical purposes. Arsenates give very similar reactions to phosphates, and are likely to be mistaken for them without due care.

Magnesia mixture, that is a solution of magnesium chloride or sulphate with ammonium chloride and ammonia, gives from aqueous solutions of phosphates a white precipitate, which is highly crystalline if it forms slowly, of ammonium magnesium phosphate $(AmMgPO_4)$.* The precipitation is complete only after standing for some hours or agitating for a shorter time; a dilute solution of a phosphate is therefore not precipitated at once. The precipitate is readily soluble in acids, even acetic acid, and reprecipitated on adding ammonia.

Barium chloride $(BaCl_2)$ gives a white precipitate of barium hydrogen phosphate $(BaHPO_4)$, readily soluble in hydrochloric or nitric acids.*

Calcium chloride $(CaCl_2)$, or even *calcium sulphate* $(CaSO_4)$ gives a white precipitate of calcium phosphate $(Ca_3P_2O_8)$ which is readily soluble in dilute acids.*

Silver nitrate $(AgNO_3)$ gives a yellow precipitate of silver phosphate (Ag_3PO_4) soluble in either nitric acid or ammonia.*

Ammonium molybdate (Am_2MoO_4) added in considerable excess to a solution containing a phosphate that has been mixed with strong nitric acid, gives on warming a light yellow precipitate of ammonium phosphomolybdate.* The precipitate is readily soluble in ammonia, and from this solution the characteristic precipitate given by mag-

nesia mixture may be obtained.   This reaction is exceedingly useful, as it will reveal the minutest trace of a phosphate, and almost all phosphates are soluble in nitric acid.

Ferric chloride (Fe_2Cl_6) gives a yellowish white precipitate of ferric phosphate ($Fe_2P_2O_8$),* which is insoluble in acetic acid, but soluble in hydrochloric acid.   It is soluble to a considerable extent in ferric acetate, and also in sodium phosphate, but not in ferrous acetate.

These last two reactions and the properties of the precipitates are of great importance, as it is by means of them that phosphates are detected and the acid radical separated from the metals that it is combined with.

PYROPHOSPHATES ($M'_4P_2O_7$) differ from orthophosphates in giving a white instead of a yellow precipitate with silver nitrate and in giving no precipitate with ammonium molybdate.   The silver pyrophosphate ($Ag_4P_2O_7$) is soluble in either nitric acid or ammonia.   The nitric acid used in the molybdate test is not unlikely, especially on warming, to change some of the pyro- into ortho-phosphate ; then of course the yellow precipitate is produced.

METAPHOSPHATES ($M'PO_3$) differ from ortho- and pyrophosphates in giving a precipitate of coagulated albumen when added to white of egg solution with acetic acid, and in giving no precipitate with magnesia mixture.   Silver nitrate gives with them a white precipitate.

THE EXAMINATION OF GROUP III.a PRECIPITATE WHEN IT CONTAINS PHOSPHATES

Phosphoric acid does not interfere with the action of sulphuretted hydrogen, so that the metals of Group II. are easily separated in the ordinary manner, whether or not they occur as phosphates or in the presence of phos-

phates.   But on proceeding to Group III., the addition of
ammonia, if a phosphate is present, precipitates the phos-
phates of the metals of Groups III., IV. and magnesium, just
as magnesium phosphate is precipitated by sodium phos-
phate in the presence of ammonia in the usual test for
that metal.   Nickel, cobalt, zinc and manganese are par-
tially precipitated as phosphates by ammonia in the
presence of a phosphate, and the remainder of these
metals is found in the filtrate from the ammonia precipi-
tate in the usual manner.   In the presence of sufficient
phosphoric acid the other metals are precipitated almost
completely; but if the phosphoric acid is deficient in
quantity, some will remain in the solution and are recog-
nised as usual.

The ammonia precipitate, therefore, when phosphates
are present, may contain all the metals of Groups III., IV.
and magnesium as phosphates in addition to the hydrates of
iron, chromium and aluminium; and it is necessary to
separate the phosphoric acid radical from the metals
before they can be treated for individual recognition in a
systematic manner.   The precipitate is soluble in hydro-
chloric acid as a whole.   If to this solution sodium acetate
is added, the hydrochloric acid is replaced by acetic acid,
thus:—

$$HCl + Na(C_2H_3O_2) = NaCl + H(C_2H_3O_2).$$
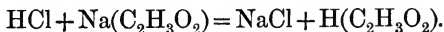
Ferric and aluminium phosphates are insoluble in acetic
acid, and if either of these metals is present a precipitate is
produced, unless iron is present in excess, when a red solu-
tion is produced because of the ferric acetate formed, and
then the ferric phosphate will probably remain in solution;
but by heating, the excess of iron (and alumina) is precipi-
tated as basic acetate, and with it the phosphate of iron.
The precipitate so obtained should contain all the iron

(and generally all the aluminium) present in the original solution, and perhaps some or all of the chromium. These metals, whether precipitated as phosphates or not, may be separated by the usual method, because aluminium phosphate behaves like aluminium hydrate in dissolving in caustic soda, and by fusion with fusion mixture and nitre, chromium as either oxide or phosphate is oxidised to a chromate, and ferric phosphate is decomposed and leaves ferric oxide.

Thus the iron and aluminium (and perhaps chromium) carry down some of the phosphoric acid radical in an acetic acid solution. If in suitable quantity they will remove the whole of it, and then the remaining metals are identified as usual. If iron and aluminium (and chromium) are absent from the original substance, obviously all the phosphates remain present in the solution.

If any (or all) of the phosphates remain undecomposed, ferric chloride is added until the liquid just becomes red from the production of ferric acetate. No ferric acetate, (therefore no red colour) will be produced until enough iron salt has been added to decompose all the phosphates with formation of ferric phosphate, so that the red colour indicates that a little excess of ferric chloride has been added. By boiling, the ferric acetate is precipitated as a basic salt, and the phosphate and basic acetate of iron are filtered off together. The solution contains now chlorides only of the metals, and their identification is proceeded with as usual.

In removing the phosphoric acid radical by means of ferric chloride in an acetic acid solution, it is necessary to precipitate all the iron from the acid solution. There must be no ferric acetate (which shows itself by its red colour) left in the solution with the idea that ammonia will get rid of it, for ferric acetate dissolves ferric

phosphate very appreciably, and on adding ammonia to a solution containing these salts ammonium phosphate is formed; and this of course will precipitate as phosphates the alkaline earths and magnesium along with the ferric hydrate. Calcium when present is often entirely lost in this manner. The filtrate from the ferric chloride precipitate must be quite free from the red colour due to ferric acetate before ammonia is added to it.

In some special cases it is possible to detect certain metals, although they are present as phosphates, by other methods. Iron, zinc, manganese, nickel, and cobalt phosphates are converted into sulphides, with formation of ammonium phosphate, by treating them with ammonium sulphide. Barium phosphate may be dissolved in hydrochloric acid and the barium precipitated as sulphate. Calcium phosphate may be dissolved in acetic acid, and then ammonium oxalate added to the solution will precipitate the calcium as oxalate. This method is useful in testing for calcium in a precipitate that is supposed to be magnesium phosphate. It is dissolved in acetic acid and the oxalate added; if no precipitate is produced, it shows the absence of calcium.

A general method of separating the phosphoric acid radical from metallic phosphates is to dissolve them in strong nitric acid and to add metallic tin, and heating to form the insoluble metastannic acid, which carries down with itself all the phosphoric acid present, leaving the metals as nitrates. After dilution and filtration the tin is got rid of from the solution by means of sulphuretted hydrogen, and the examination for the metals is continued as usual.

COMPARATIVE REMARKS ON THE ACIDS

Sometimes a single free acid may require identification, and then it is not always necessary to test as if a salt of the acid were being dealt with.

Carbonic and sulphurous acids are for all practical purposes merely a solution of the anhydrides in water. A solution of calcium or barium hydrate precipitates both. Sulphurous acid has a characteristic odour, and it strongly reddens blue litmus paper. Carbonic acid has hardly any odour at all, and turns blue litmus paper only half-way towards red.

Hydrochloric, hydrobromic, hydriodic, and hydrofluoric acids, and sulphuretted hydrogen, are themselves gases, but are often preserved and used as solutions in water. The halogen acids dissolve very largely in water, and produce liquids of exceedingly acid characteristics and that fume when exposed to the air. Sulphuretted hydrogen is rather a weak acid, and is at once recognised by its odour.

Nitric and sulphuric acids are highly corrosive and heavy liquids. Sulphuric acid is of an oily consistency. Nitric acid is recognised at once by the red fumes evolved when a fragment of copper is dropped into it, and by the fact that the metal dissolves. Neither sulphuric nor hydrochloric acid will dissolve copper or give off red fumes.

Boric, silicic and phosphoric acids are solid substances. They are weak acids, for their salts with the alkali metals have an alkaline reaction.   But at high temperatures their anhydrides can displace even sulphuric anhydride from sulphates, because they are not so volatile as it is. Silicic acid is so weak an acid at ordinary temperatures that even the carbonic anhydride in the air will displace it from solutions of its alkaline salts, and ammonia, instead of combining with it as it does with other acids, precipitates it from its solution in acids.   At ordinary temperatures silicic acid has hardly any of the properties by which acids as a class are distinguished, but at high temperatures its anhydride will attack the salts of almost any of the others.

Sulphates are the only salts, except silicofluorides, that give a precipitate with barium chloride in a solution acidulated with hydrochloric acid that is insoluble on adding more hydrochloric acid and on boiling.

Chlorides, bromides, and iodides are the only salts (except sulphides) that will give a precipitate with silver nitrate from a solution acidulated with nitric acid that is insoluble on adding more nitric acid.   The precipitate given by sulphides is black, and so easily distinguished from the others.

Iodides are distinguished from all other salts by the blue colour produced with starch when iodine is set free from them.

Nitrates and chlorates give no precipitates by double decomposition.   They cause deflagration when heated on charcoal, but the instability of chloric acid, and the explosive violence of the decomposition of the chloric peroxide liberated when a chlorate is dropped in minute fragments into warm sulphuric acid, at once distinguish a chlorate.   Nitrates are distinguished by their oxidising

power and the products of their decomposition, whether oxygen, nitric oxide (which imparts a brown colour to a solution of ferrous sulphate), or nitrous fumes (recognised by their red colour).

Fluorides are characterised by the unique power possessed by the liberated hydrofluoric acid of forming a gas containing silicon by its action at ordinary temperatures on silica or silicates.   The silica fluoride itself may be recognised by the detection of the silica it contains, or the volatilisation of the silica from the silicate may be ascertained by the etching test.

A METHOD OF ANALYSIS

The tables that follow here consist of a selection of the reactions that have been already given in detail, so arranged so as to form a method or system of analysis. The method here given is not the only possible method, but it should be observed that it is a method and not a mere series of experiments. There is always a definite reason for the order of the items of the work, and if this order is not observed, so far as this method is concerned the result is irregularity, the thing above all others that is to be avoided.

In working exercises according to these directions, it should be always borne in mind that the aim of these exercises is not the finding out what may be present in the substance given; this may be known by the teacher beforehand. The aim of the work is to gain experience in the best ways of performing analyses. A dozen exercises may be done, and the end results may be correct in every one, but the time spent on them will be worse than wasted if the method or order of the work has been bad. The use of such exercises as are given in the laboratory is to the would-be chemist exactly what the practising of exercises and scales is to the young musician. The aim is not merely to perform the exercise, but to do it in such

a manner that it shall be practice in a thoroughly sound method of work. It is far better for the beginner to work a good method badly than a bad method (or no method) successfully; because in the first case practice will give proficiency, but in the second case no amount of work will obviate the confusion and uncertainty which is inseparable from working on a bad foundation.

The beginner should at first follow the methods given exactly; but after a few exercises he may be able to occasionally substitute a modification of some detail that will, in the particular case in hand, lead more directly to the result. In all such variations it is important that the student should be able to clearly point out exactly why he departs from the method given, and what advantage he gains by doing so.

The work is divided into four main sections. First, a general preliminary examination, chiefly by dry methods; and this it should be noted is quite as systematic as any other part of the work. It is not a mere series of experiments, but each follows the other for a definite reason. The second section consists of the examination of a solution for the basic (or metallic) radicals, but includes one or two of the acid radicals that must be considered because their presence interferes with the work. Then follows a preliminary examination for the acid radicals, and then a final examination for those acid radicals that may possibly be present.

After the result is obtained, a general review of the work is made, and the obvious properties of the original substance are accounted for by a distinct statement of all those constituents that may be present that have the observed properties.

The method that is elaborated in these tables applies especially to salts or oxides or mixtures of these—the kind

of exercise that is always first given to the student ; and it supposes also that the substance is soluble either in water or acids. The treatment of insoluble substances or residues, and of alloys and minerals so far as they may with advantage receive different treatment, is dealt with in sections immediately following the tables. Then follow some suggestions for making notes of the work, and a specimen record of an analysis.

THE TITLE

Before beginning any piece of work a concise and distinctive title should be set down. The following are a few examples— "Examination of a white powder;" "Examination of a red pasty mass;" "Examination of a deliquescent white powder that has an odour of ammonia;" "Examination of a mixture of coarsely-powdered blue and white substances;" "Examination of a hard black mineral;" "Examination of a grey metallic substance."

Negative statements should be avoided in a general title. "Colourless" is a word that rarely, if ever, need be used; it is preferable to write "white" or "black," or "transparent" or "glass-like." The reason for the omission of negative statements from a general title is not only that it is desirable to say what the work or substance is rather than what it is not, but that it is rarely possible to make a complete negative description. There is no special reason why the absence of one property should be stated rather than the absence of other properties.

The title should be written boldly so that it may clearly indicate the beginning of the exercise, and if it does not begin a fresh page in the note book, there should be a conspicuous space left between it and the end of the previous exercise.

THE PRELIMINARY EXAMINATION

THE preliminary examination is performed by heating the substance and noticing how it is affected. The heating is done in three stages—(1) in a bulb tube, (2) on charcoal, (3) on a platinum wire. In the first the temperature is equal to a medium or low red heat; in the second it is sufficient to easily fuse a large bead of silver; in the third it is almost high enough to fuse platinum. Of course the temperature of the flame is not altered appreciably, if at all; but these are approximately the temperatures to which the substance under examination is actually raised. In the first the support for the substance is of a retort-like or semi-enclosed character; in the second it is a surface—entirely open; in the third the surface is done away with as much as possible, and the support is the nearest practical approach to a geometric line. The thinness of the platinum wire is limited by the softening or possible fusion of it in the flame. The results of these primary tests lead in some cases to secondary or confirmatory tests, and these are indicated in the experiment column if a new experiment is necessary, or in the observation column if it is merely a continuation of the first experiment.

The student should not be guided as to his observations by those set down in the table. He should perform the experiment and make his own observations as the changes proceed, and then set down the account of them exactly in the order in which they took place. No negative observation should be recorded in connection with a general experiment. He should then, by reference to the table, see whether any of his observations lead to secondary experiments; if so, these should be performed and the results recorded before going on to the next main experiment.

The symbol for an element or a radical refers generally to compounds containing that element or radical. The formula of a compound refers to the specific substance mentioned.

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THE PRELIMINARY EXAMINATION

Experiment.	Observation.	Inference.
1. HEAT A LITTLE OF THE SUBSTANCE IN A BULB-TUBE HELD HORIZONTALLY IN THE FINGERS.	Decrepitation.	K_2SO_4, PbN_2O_6, NaCl, and many other compounds. (Decrepitation is due to the physical condition, and its extent will vary with different samples of the same compound).
	Fusion.	Salts of K and Na (the normal sulphates require a high temperature), and some salts of Ba, Sr and Ca, &c. Nitrates, and salts containing water of crystallisation.
	Volatilisation.	
	Water, condensing in drops.	Water of crystallisation, or of hydration, or mere uncombined moisture.
	Sublimates.	
	White.	Am, Hg, As, less often Sb, Cd, &c. (HF liberated from moist fluorides may corrode the glass; but this effect does not disappear on heating it).
	Yellow.	As_2S_3. HgO often accompanies metallic mercury.
	Yellow but becomes red when rubbed.	HgI_2.

Experiment.	Observation.	Inference.
	Black (or steel grey) but becomes red when rubbed or ground, and deposits near the heated part of the tube.	HgS.
	Steel grey with a violet vapour.	Iodine, free or from iodides.
	Colourless, transparent, heavy drops.	SO_3 from sulphates of heavy metals, alkaline bisulphates, &c.
	Reddish brown drops yellow and solid when cold.	S free or from some sulphides (as FeS_2), from some thiosulphates, &c.
	Metallic drops.	Hg from its salts with oxyacids, often mixed with yellow HgO.
	Gases.	
	Colourless and odourless.	
	Relights a glowing splinter.	Oxygen from some oxides, nitrates, chlorates, &c.
	Turns lime water turbid.	CO_2 from carbonates of heavy metals, bicarbonates, &c.
	Nitrogen (has no distinctive reaction).	From an ammonium salt in the presence of a nitrite, hypochlorite, &c.

Experiment.	Observation.	Inference.
	Colourless, but has an odour.	
	Odour of ammonia and is alkaline to litmus paper.	NH_3 from ammonium salts.
	Odour of burning sulphur and is acid to litmus paper.	SO_2 from sulphites, or from sulphates of heavy metals.
	Odour not distinctive and is acid to litmus paper.	HCl from some chlorides when moist.
	Bleaches litmus paper.	Chlorine from chlorates, &c.
	Odour of rotten eggs.	SH_2 from some sulphides when moist.
	Coloured.	
	Red fumes which redden litmus paper.	Nitrous fumes from nitrates of other than alkali metals.
	Red fumes which bleach litmus paper.	Bromine from some bromides or nitrous fumes mixed with chlorine.
	Violet fumes.	Iodine from some iodides.
	The Residue.	
	White.	In general, the absence of substances that give definite colours.
	White, but yellow when hot.	ZnO.

Experiment.	Observation.	Inference.
	Yellow, yellowish brown hot.	SnO_2.
	Yellow, reddish brown hot.	PbO, Bi_2O_3.
	Reddish brown, nearly black when hot.	Fe_2O_3.
	Brown.	Mn_3O_4.
	Black.	CuO, Co_3O_4. The above oxides may have been present in the original substance, or may have been produced from salts by the heating.
	Fusible.	Salts of K and Na, some salts of Ba, Sr and Ca, some chlorides of heavy metals, &c.
	Infusible.	Sulphates of K and Na and innumerable other substances.
If mercury or arsenic has been indicated, but not conclusively, grind the substance with about an equal bulk of KCy and six times its bulk of dry Na_2CO_3, and heat the mixture in a bulb-tube.	A black sublimate with a garlic odour. A sublimate of metallic globules.	As. Hg.
If volatile matter is present, other than water, grind a little of the substance with soda lime, moistening the mixture with water.	An odour of NH_3 is given off, and the gas is alkaline to litmus paper.	Am. This test is final for the presence or absence of Am.

Experiment.	*Observation.*	*Inference.*
2. HEAT A LITTLE OF THE SUBSTANCE IN A SMALL CAVITY ON CHARCOAL BEFORE THE BLOWPIPE FLAME. If the substance decrepitates obstinately, it must be ground finer, or even moistened.	**Decrepitation.**	K_2SO_4, PbN_2O_6, NaCl and many other salts.
	Fusion. This fusion is after the water, if any, has been driven off.	Salts of the alkalies, some salts of the alkaline earths, &c.
	Deflagration.	Nitrates, nitrites, chlorates.
	Fumes. other than those referred to in connection with the reducible metals given below are best dealt with by means of the bulb-tube.	
	The Residue.	
	White and infusible.	Mg, Ba, Sr, Ca, Zn, Al, &c.
	Coloured.	Mn, Ni, Co, Fe, Cr, Cu, &c.
	Metallic, showing small beads or other evidence of a metal.	Ag, Sn, Pb, Bi, Sb, Cu, Fe, Ni, Co.

Experiment.	*Observation.*		*Inference.*
If the residue is not white, heat a little of the original substance in a borax bead in both flames.	The bead is coloured.		
	Oxidising flame.	*Reducing flame.*	
	Reddish brown.	Colourless.	Mn.
	Reddish brown.	Grey (turbid).	Ni.
	Blue.	Blue.	Co.
	Yellow (red when hot).	Green (bottle).	Fe.
	Green.	Green.	Cr.
	Green to blue.	Red (turbid).	Cu.
If there is evidence that a metal has been reduced, grind some of the substance with about an equal bulk of KCy and six times its bulk of fusion mixture, and heat the mixture on charcoal, adding more flux if necessary.	A brilliant white bead of metal, malleable, rather hard.		Ag.
	A white bead, brittle, with a yellow incrustation.		Bi.
	A white bead, brittle, with a white incrustation which probably covers the bead.		Sb.
	A white bead, malleable, with a slight yellow incrustation.		Sn.
	A greyish white bead, malleable, soft enough to mark paper.		Pb.
	Red beads very difficult to fuse together, or merely a red mass.		Cu.

Experiment.	Observation.	Inference.
	Grey infusible powder, that is magnetic.	Fe, Ni, Co.
The following also may be noticed in connection with this test although there is no visible indication of reduction to the metallic condition.	No beads, but an incrustation that is yellow hot and white cold.	Zn.
	No beads, but a reddish brown incrustation.	Cd.
	Garlic odour and perhaps a white very volatile incrustation.	As.
3. HEAT A LITTLE OF THE SUBSTANCE, ON A FINE PLATINUM WIRE, IN THE LOWER HOTTEST PART OF THE BUNSEN FLAME.	*The flame is coloured.*	
	Luminously yellow	Na.
	Bluish.	K, As, Sb, Pb, $CuCl_2$.
	Violet.	K.
	Green.	Cu, Ba, B_2O_3, $MnCl_2$.
	Red.	Ca.
	Crimson.	Sr.

EXAMINATION OF A SOLUTION FOR THE BASIC (OR METALLIC) RADICALS.

To prepare the Solution

IF the substance is not already in a state of fine division it is generally advisable to grind it in a mortar.

A little of the powder should then be put on to a piece of moist litmus paper, and after a few seconds washed off. The reaction acid, alkaline, or neutral should be noted.

The quantity that should be taken for the solution is from a half to one gram, that is about as much as could be scooped up by a threepenny piece if the powder is of a moderate specific gravity, more by bulk of a light powder and very much less of a very heavy powder, such as lead or mercury sulphides. It is not necessary to weigh out the portion taken. It is put into a test tube, water is added to about a quarter fill the tube, and it is warmed. If the substance dissolves completely the solution is ready to proceed with.

If it does not dissolve, a drop or two of the clear liquid is evaporated to dryness on a watch glass to see whether any has dissolved, unless it has already been proved that the substance is partly soluble in water by the reaction that it shows on moistened litmus paper. If the substance is partly soluble in water, the colour (if any) of the solution, and the colour of the residue should be noted. Many a coloured substance may be traced through the various operations, and such knowledge as can be obtained in this way is necessary, or if neglected the work

is incomplete. Next, add two or three drops of strong hydrochloric acid and warm, if necessary add more acid, but not more than equal to about a tenth of the bulk of the water. In any case use as little acid as possible, and if the substance completely dissolves, note that it dissolves in dilute hydrochloric acid, and proceed.

If it does not completely dissolve in either water or dilute hydrochloric acid, start afresh with a new quantity of the substance, pour over it in a test tube about four or five times its bulk of strong hydrochloric acid, mix the acid and the powder by shaking a little, and then heat the mixture until about half the acid has evaporated away. Add water to about one-third fill the tube and warm if necessary. If the solution is complete, note that the substance dissolves in strong hydrochloric acid (or, more correctly speaking, is made soluble by strong hydrochloric acid) and proceed.

If the substance still does not entirely dissolve, and if from the appearance of the residue and the results of the preliminary examination it is judged that the action of the hydrochloric acid has been incomplete, let the residue subside, pour off the solution, and treat the residue again as described.

What fails to dissolve by this means is to be considered insoluble and treated as afterwards described, the solution of the soluble part being proceeded with as if it were the solution of the whole substance, unless from the preliminary examination or the colour of the residue it is known to be something that is soluble in aqua regia. In this case the residue alone may be treated with as little aqua regia as possible to effect its solution, excess of the acids evaporated off, and the solution added to the solution already obtained. Sometimes, however, it is worth while (indeed preferable) to keep the part which dissolves only in aqua regia separate from the other, because there are so few things that it is likely to be, and examine it by itself. This applies especially to arsenic compounds, such as sulphide of arsenic, as arsenic acid in an ordinary solution for bases is troublesome to reduce, but by itself it can easily be identified. Aqua regia should never be used unless it is known exactly why it is necessary or desirable.

The following exceptions to the process described above for preparing the solution are founded on the knowledge obtained in the preliminary examination.

If iodine or bromine is present, especially iodine, whether the substance dissolves wholly in water or not, it is advisable to get rid of it by warming the substance with hydrochloric acid and adding strong nitric acid a drop at a time, and boiling. The operation may be done in a small porcelain dish.

If a chromate is present, it is desirable to boil the substance in a little strong hydrochloric acid and then to dilute, whether or not it dissolves wholly in water. This reduces the chromate with formation of a chromic salt, and so prevents the precipitation of much sulphur when sulphuretted hydrogen is passed.

Nitrites and hypochlorites may be treated in the same way and for a similar reason.

If antimony or bismuth is present, the solution in hydrochloric acid may give a white precipitate of oxychloride on the addition of water. It should then be noticed whether the solution is complete before adding the full amount of water. If so, the sulphuretted hydrogen may be passed and the full amount of water added afterwards, then passing more gas ; or the full amount of water may be added, and the precipitated oxychlorides disregarded, as sulphuretted hydrogen will convert them into sulphides if the treatment with the gas is thoroughly carried out.

The following matters may be noticed, though they do not lead to exceptional treatment.

If a mercurous salt is present and the substance does not dissolve in water, the hydrochloric acid used will precipitate mercurous chloride. In this case aqua regia is needed. The addition of one or two drops of concentrated nitric acid to the hot liquid is often sufficient.

If silver is present under the same circumstances, it will be converted into silver chloride, and this will remain with the insoluble residue. The treatment of this is considered in the subsequent section on the examination of insoluble residues.

If lead is present and hydrochloric acid has to be used in making the solution, on adding water and cooling, lead chloride often crystallises out. The crystals are so characteristic that they are at once identified and treated as a Group I precipitate.

In carrying out the directions given in the tables, constant reference should be made to the detailed descriptions of the reactions involved given in the earlier

part of the book, and the exact changes that take place should in every case be carefully followed through.

Every reagent that is set down to be added must be added in sufficient quantity to produce the required change completely. It is generally desirable, after having produced a precipitate, to add a little more of the reagent to make sure that the whole of the substance that is to be precipitated has been removed from the solution.

To the solution add a few drops of dilute HCl, and if a precipitate is produced add the acid until a

A white precipitate. Group 1 is present. The oxychlorides of Bi, Sb, and more rarely Sn, may be precipitated here as granular white precipitates. They readily dissolve on adding more acid. If their solubility in acid has been proved by testing a drop or two, it will be better to let the precipitate remain than to add a large quantity of acid. If the solution of the original substance has an alkaline reaction, other substances may be precipitated here. This circumstance is dealt with in a section following these tables.	Solution. Pass H₂S* as long as a precipitate is produced, and of the filtrate should be much diluted, and if more precipitate is pr

Solution. Pass H_2S* as long as a precipitate is produced, and of the filtrate should be much diluted, and if more precipitate is pr

A black, brown, orange or yellow precipitate. Group 2 is present. A fine white precipitate that does not settle down is sulphur only, produced by oxidation of the H_2S, as by a ferric salt. Arsenic acid gives a precipitate slowly : it is often better to reduce the arsenic acid first by means of sulphurous acid. If a white precipitate of $BaSO_4$ or $SrSO_4$ is produced during the reduction, it must be examined by the method given for insoluble residues. A brick-red precipitate shows that probably lead is present and that the solution is too acid. In this case dilute the solution.	Solution. Evaporate in a c by adding two or three drops solution to dryness to separate t Take a few drops of the prepa and gently warm. A yellow pre To the remainder of the solut boiling up once more its odour i A white, green or reddis brown precipitate. Group 3A is present. If phosphates are present a the metals of Groups 3 and 4 an Mg may be in this precipitate thrown down as phosphates. A special table is given fo the examination of this precipi tate when phosphates are present Group 3C.

* If Group 2. is probably absent, H_2S may be passed through a few drops of the solution with the precautions stated. be boiled off, and iron, if in the ferric condition, is not reduced.

p more gives no further precipitate.

arm gently. After filtering, H₂S must be passed again to ensure a complete action. Then a drop or two
uced the whole must be diluted.

1 till the H₂S has been boiled off. If iron is suspected, any ferrous salt must be oxidised to ferric
a sufficiency) of strong nitric acid, and heating again. If a soluble silicate is suspected, evaporate the
silica and extract the residue with HCl and water.
d solution, add to it an equal bulk of strong HNO_3 and about six times the bulk of ammonium molybdate
itate shows that phosphates are present.
1 add a considerable quantity of AmCl, transfer it to a small flask, heat to boiling, add AmOH until after
erceptible, and filter at once.

Solution. At once pass H₂S, or manganese if present will be oxidised and precipitated as
manganic hydrate.

A white, salmon-coloured or black precipitate. Group 3B is present.	Solution. Add AmOH unless the solution smells of NH₃, a slight excess of Am_2CO_3, and warm gently.	
The yellow cadmium sulphide will come here if cadmium is present and not completely precipitated in Group 2.	A white precipitate. Group 4 is present.	Solution. To be examined for Group 5.

f no precipitate is produced, the remainder of the solution is proceeded with without passing H₂S, the gas has not then to

The precipitate may contain Hg_2Cl, $AgCl_2$ and $PbCl_2$. Pour boiling water over it as it is on the filter.

Residue. Warm gently with dilute AmOH.

| The Residue is black. Dry it, mix it with Na_2CO_3 and heat the mixture in a bulb tube.
A sublimate of metallic globules.
Hg is present. | Solution. Acidify it with HNO
A white curdy precipitate.
Ag is present.
If mercury is present some of the sil- |

The precipitate may contain Hg, Pb, Bi, Cu, Cd, Sn, Sb and As as sulphides. Wash and then transfer dilute and filter. (If mercury is present it is better to use yellow ammonium sulphide, as HgS is appreci

Residue. Wash well, transfer the wet precipitate to a test-tube, pour on to it an equal bulk of strong HNO_3, heat till red fumes are no longer visible in the lower part of the tube, add water. Add dilute H_2SO_4, and alcohol equal in bulk to the whole liquid, unless by testing a drop or two first these reagents are found to give no precipitate.

Residue. Warm with ammonium acetate to dissolve the $PbSO_4$.		Solution. Copper if present colours the solution green. Evaporate off the alcohol, if it has had to be added, add excess of AmOH and warm.	
Residue. Whether white or black must be tested for mercury. If only semi-fused globules of sulphur it may be neglected. Mix with dry Na_2CO_3 and heat in a bulb-tube. A sublimate of metallic globules. Hg is present.	Solution. Add K_2CrO_4. A yellow precipitate. Pb is present. Lead is always found here if present in Group 1, because HCl cannot completely precipitate it.	Precipitate is white. Dissolve it in a few drops of dilute HCl and pour the solution into a large bulk of water. A white precipitate. Bi is present.	Solution. If colourless, copper is absent, then pass H_2S to test for cadmium. If blue, divide into two parts.
		1. Add acetic acid till acid and K_4FeCy_6. A chocolate brown precipitate. Cu is present.	2. Add KCy till colourless and pass H_2S. A yellow precipitate. Cd is present.

Solution. On cooling white needle-shaped crystals of $PbCl_2$ separate. Add K_2CrO_4.
A yellow precipitate.
Pb is present.

always remains in the black residue.

e wet precipitate to a test-tube, pour over it two or three times its bulk of caustic soda, warm well,
y soluble in caustic soda.)

Solution. Add HCl to reprecipitate the sulphides. To the moist precipitate add strong HCl and
il until H_2S ceases to be evolved. Add water.

Residue. Mix with KCy and Na_2CO_3 and heat in a bulb-be.	Solution. Pour into a porcelain dish, put in a piece of platinum foil and a piece of zinc that touches the foil.	
A steel-coloured sublimate and grlic odour. As is present.	The platinum foil is covered with a dark deposit. Sb is present.	The solution after the platinum is removed must be allowed to act on zinc until the acid is exhausted. The clear liquid is poured away and the residue and precipitate (if any large pieces of zinc remain they may be removed after what adheres to them has been scraped off) are dissolved in a little strong HCl, putting in a piece of platinum foil to assist the solution, water is added and then $HgCl_2$. A white precipitate of Hg_2Cl_2 or a grey precipitate of mercury is obtained if Sn is present.
f Am_2S_2 has been used in the first instance and this precipitate therefore contains much sulphur, it is better to dissolve it in a little aqua regia and employ Reinsch's test, instead of heating in the tube as above.		

EXAMINATION OF THE PRECIPITATE PRODUCED FOR GROUP IIIa.

The precipitate may contain Fe, Cr and Al as hydrates. Dissolve it in dilute HCl: a small quantity of acid may be passed a few times through the filter to effect solution. Iron gives a yellow solution, chromium a deep green. Add an excess of caustic soda, and boil.

Precipitate. Dry, fuse with fusion mixture and a little KNO_3 on platinum foil. Boil the residue with water.		Solution. Add just enough litmus solution to tint it blue. Then acidify with HCl, add AmOH till it is just alkaline, and warm.
Residue is brownish-red Fe_2O_3. Dissolve in dilute HCl, add K_4FeCy_6. A dark blue precipitate. Fe is present. A slight white residue is often obtained here when iron is absent if an alkaline earth is present with fluorides, or more rarely borates. In the absence of iron and chromium, this appears as a precipitate with AmOH, which ... in NaOH and there- ... uminium. Such a ... identified. CaF_2 ... composed by fusion ... re.	Solution is yellow if chromium is present. Add excess of acetic acid and lead acetate. A yellow precipitate. Cr is present. If manganese is present the fused mass on the platinum foil will be green. This green colour if present should be noted as evidence of the presence of manganese, but the chief bulk of this metal should be found in Group 3B.	A white precipitate, but tinted blue by the litmus if that is used. Al is present. The caustic soda solution should be tested alone, as it may contain silica or alumina in solution, which would be precipitated.

The precipitate may contain Zn, Mn, Ni and Co as sulphides. If it contains no sign of blackness Ni and Co are absent, and only Zn and Mn need be looked for. In this case dissolve it by pouring hot dilute HCl on to the filter, boil to get rid of H_2S, dilute and proceed as below.

If black, remove the precipitate to a test-tube, add a little dilute HCl and boil (the black NiS and CoS remain but little attacked), add a small crystal of $KClO_3$ and boil, repeating if necessary till only sulphur remains. Boil off the chlorine, add a little water and filter. (The liquid containing free chlorine must not be allowed to come into contact with the filter paper, or organic matter will be introduced into the solution and the NaOH will then not completely precipitate the hydrates of Ni and Co.)

The solution if green contains Ni, if red, Co. The two metals together in certain proportions give an almost colourless solution. Add excess of NaOH, warm, dilute and filter.

Precipitate. Dissolve in the least quantity of dilute HCl. If some $Mn(OH)_2$ has become oxidised by exposure, a drop or two of sulphurous acid will dissolve the dark brown manganic hydrate at once. Add excess of ammonium acetate, that there may be no free acid but acetic present and pass H_2S.		Solution. Pass H_2S, a white precipitate. Zn is present.
Precipitate. Remove the black sulphides to a test-tube, dissolve in a little hot dilute HCl by the aid of $KClO_3$, boil off the chlorine, add solid Na_2CO_3 till a permanent precipitate is just produced and then a drop of HCl to redissolve it (this gets rid of the excess of free acid), add a solution of KCy till the precipitate at first produced is redissolved, boil, cool, add an equal bulk of NaOCl solution and warm gently.		Solution. Add AmCl and AmOH, and pass more H_2S if necessary. A salmon-coloured precipitate. Mn is present.
Precipitate is black $Ni_2(OH)_6$. Confirm on a borax bead. Ni is present. If Ni is not precipitated as it ought to be, try a small quantity of the solution with more NaOCl, and if this gives a precipitate the whole solution must be so treated.	Solution. Evaporate a few drops to dryness and heat the residue on a borax bead. A blue bead. Co is present.	

The precipitate may contain Fe, Cr and Al as hydrates, and all the metals of Groups 3 and 4 and Mg
used nearly neutralise with Na_2CO_3, using the solid to prevent much increase in the bulk. Cool, add ab
If the solution is red there is more than sufficient iron to combine with all the phosphoric acid radical
Boil and filter at once. If the solution was red, the heating must be continued until all the ferric ace

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Precipitate consists of phosphates or basic acetates of iron and aluminium and perhaps chromium.

Examine it for Fe, Cr and Al according to the method given for Group 3A.

This precipitate may contain some phosphates of the alkaline earths due to an insufficiency of acetic acid to hold them in solution. If so, dissolve it in dilute HCl and add acetic acid mixture again.

The reference to alkaline earthy fluorides given in Group 3A applies here also.

All the iron present in the substance is precipitated here and probably all the aluminium. Probably most of the chromium will remain in the solution.

Solution. Any phosphoric acid radical remaining must next be
has been removed in the Fe, Cr and Al precipitate. If no precip
of these conditions holds, take about a tenth part of the solutio
phosphates remain.

If no phosphates remain proceed at once to add AmCl and AmOH
If phosphates are still present in this solution, add Fe_2Cl_6 a droj
ferric acetate and filter at once.

Precipitate is ferric phosphate and basic ferric acetate.

Neglect it.

If Al or Cr remained in the solution it is just possible that some of them might be brought down here with the iron salts, but this very rarely happens.

Solution. This solution must
(Ferric phosphate is soluble in fe
Add AmCl, heat and add AmC

Precipitate of aluminium and chromium hydrates that remained in solution before.

Examine it for these metals by dissolving it in dilute HCl, adding excess of NaOH, &c.

ing present.

phosphates. Dissolve in dilute HCl, using the least possible quantity of acid; if much acid has to be
an equal bulk of the mixture of sodium acetate and acetic acid.

te is precipitated, and the solution is consequently free from the colour due to this salt.

moved. If iron was present in excess (the acetate giving a red colour), the phosphoric acid radical
te was produced by the acetate, obviously all the phosphates remain in this solution. If neither
and add one drop of a dilute solution of Fe_2Cl_6—a red colour due to ferric acetate shows that no

en H_2S, and so on as below.
a time until no more precipitate is produced and the solution is tinged red. Heat to precipitate the

e free from the red colour due to ferric acetate. If it is not it must be boiled and filtered again.
acetate, it can therefore only be thoroughly precipitated by completely precipitating the acetate.)

Solution. Pass H_2S.

Precipitate consists of the sulphides of Zn, Mn, Ni and Co—these metals having been at first precipitated as phosphates. Examine it as directed for Group 3B.	Solution. Add AmOH, if necessary, and Am_2CO_3 and warm.	
	Precipitate consists of Ba, Sr and Ca carbonates—the metals having been at first precipitated as phosphates. Examine it as directed for Group 4.	Solution. Add HNa_2PO_4. A white precipitate. Mg is present, originally precipitated as phosphate.

EXAMINATION OF THE PRECIPITATE PRODUCED FOR GROUP IV.

The precipitate may contain Ba, Sr and Ca as carbonates.
Dissolve it in warm acetic acid (pouring the acid through the filter a few times), dilute and add K_2CrO_4.

Precipitate is yellow. Dissolve it in dilute HCl and add H_2SO_4. A white precipitate. Ba is present.	Solution. Add Am_2SO_4 and allow the solution to stand about ten minutes.

Precipitate is white. Heat it on a platinum wire after moistening it with strong HCl. It gives a crimson flame. Sr is present. A copious crystalline precipitate of calcium sulphate may fall here if much calcium is present. In this case warm the precipitate with a strong solution of Am_2SO_4 with a little AmOH. Calcium sulphate dissolves and can be tested for with ammonium oxalate.	Solution. Add ammonium oxalate. A white precipitate. Ca is present.

The solution may contain Mg, K and Na besides ammonium salts used in the work, and some of the acid radicals present in the original substance.   Divide it into two parts.

Smaller part.

Add HNa_2PO_4 and allow to stand.

A white precipitate.

Mg is present.

There will be precipitated here the phosphates of almost all the other metals that have not been completely removed.   The alkaline earths and aluminium are those that most often interfere.   If it is necessary to test for these, dissolve the precipitate in acetic acid ($Al_2P_2O_8$ will be left insoluble) and add a little Am_2SO_4 and $Am_2C_2O_4$.   Filter off any precipitate and reprecipitate the $MgAmPO_4$ by adding AmOH.

Larger part.

Evaporate to dryness in a porcelain dish.

Ignite the residue on platinum foil until all the ammonium compounds have been volatilised.

If no residue, Group 5 is absent.

If a residue, test it by heating a little on a platinum wire.

A luminously yellow flame.   Na is present.

A violet flame.   Na is absent.   K is present.

If Na is present, the blue glass may be used to look for K.

Unless K is certainly absent it must be examined for by $PtCl_4$. For this purpose, dissolve the residue in the least amount of water, with a drop of dilute HCl if necessary, in a small porcelain dish, and add $PtCl_4$.

A yellow crystalline precipitate shows that

K is present.

If no precipitate, evaporate the solution just to dryness, taking care not to over-heat any part, and to the residue add alcohol and a drop or two of water if a whitish insoluble residue appears.   The fine yellow, heavy, crystalline precipitate of potassium platinum chloride will now be seen if there is any potassium present.

THE CONDITION OF CERTAIN METALS

IF either mercury, tin, arsenic, manganese, iron or chromium has been found, the condition in which it is present should next be determined. The distinctions between the states of oxidation of these metals have already been given, but the following notes may be useful. Observe that finding a metal present in one condition does not prove that it is not present in another. Both ferrous and ferric salts may be present. A chromate and a chromic salt may be together.

Mercury.—Mercurous salts are easily converted into mercuric during the preparation of the solution if nitric acid or any other oxidiser is present. It is generally safer to test for mercurous salts by pouring some caustic soda or ammonia over some of the original substance when mercurous salts will be blackened.

Tin.—Stannous salts reduce mercuric chloride, stannic salts do not. The colour of the sulphide in the group and also when reprecipitated from its solution in caustic soda is a guide if there has been no previous opportunity for oxidation or reduction of the compound. A stannous salt added to a mixture of ferric chloride and potassium ferricyanide gives a dark blue precipitate, but many other reducing agents do the same.

Arsenic.—If present as the yellow or reddish sulphide it is of course in the arsenious condition. The manner of the precipitation of its sulphide with sulphuretted hydrogen is an important matter. Arsenates are very similar to phosphates. An ammonia extract of the original substance will contain the arsenic acid unless there are some metals present, such as the alkaline earths, which form arsenates that are not decomposed by ammonia. Arsenic acid when extracted by ammonia, that is, ammonium arsenate, may be tested for by magnesium sulphate. Arsenic acid should not be looked for by means of ammonium molybdate, because the nitric acid used might oxidise some arsenious into arsenic acid.

Manganese.—This metal is in the dyad condition except when it occurs as a peroxide or as a manganate or permanganate. The colour of the higher oxides, the chlorine given off when they are heated with strong hydrochloric acid, the insolubility of the oxides in water and their slow solubility in dilute acids, generally leave no doubt as to the character of the manganese compound present. Manganates and permanganates have such characteristic colours that they cannot pass unnoticed, and their presence is easily confirmed.

Iron.—Ferric oxide is distinguished by its reddish brown colour. Ferric salts in solution are yellow, especially when hydrochloric acid is added. An aqueous or dilute acid solution of the original substance should be tested by adding to two separate parts of it, ammonium thiocyanate and potassium ferricyanide. The first gives a red colour with ferric salts, and the second a dark blue precipitate with ferrous salts.

Chromium.—Chromic salts are green or violet, in solution with hydrochloric acid they are green. Chromates are red or yellow. By boiling with sodium carbonate, chromates are decomposed with formation of sodium chromate which is soluble in water, and chromium hydrate is precipitated from chromium salts; but this test is not infallible. Chromium may be present in the precipitate given by sodium carbonate as a basic chromate. The results of this test must therefore be regarded in conjunction with the other properties of the substance, and the colour of the precipitate that is produced by the sodium carbonate must be carefully observed if there is any doubt as to the presence of chromic salts.

THE PRELIMINARY EXAMINATION FOR ACID RADICALS

THIS, like the general preliminary examination, consists of one experiment, but in this case done in two stages, and a few secondary experiments that follow when necessary. The primary experiment consists in adding an acid to the original substance, and noticing what acids, anhydrides, or other products are thereby liberated. The reagent used is first a weak acid, and secondly a strong acid. It is obvious that the acid used must itself give off no fumes or gases under the conditions of the experiment or they would be confused with those liberated from the substance. The warming must, therefore, not be sufficient to volatilise the reagent.

Experiment.	*Observation.*	*Inference.*
1. POUR SOME DILUTE HCl OVER A LITTLE OF THE SUBSTANCE IN A TEST TUBE, AND WARM GENTLY.	Effervescence. The gas has neither colour nor odour, and precipitates lime or baryta water.	CO_2 from carbonates.
	The odour of burning sulphur, probably without effervescence. The gas precipitates baryta water, the precipitate is soluble in HCl and chlorine water added gives a white precipitate.	SO_2 from sulphites and, with precipitation of sulphur, from thiosulphates.
	The odour of rotten eggs blackening paper moistened with lead acetate.	H_2S from certain sulphides.
	Reddish brown fumes.	From nitrites.

Experiment.	Observation.	Inference.
	Chlorine, recognised by its odour and bleaching litmus paper.	From hypochlorites.
2. POUR SOME STRONG H_2SO_4 OVER A LITTLE OF THE SUBSTANCE IN A TEST TUBE AND WARM GENTLY.	Acid fumes are given off which redden litmus paper.	HCl, HNO_3, or HF from their corresponding salts.
	Chlorine is given off, bleaching moist litmus paper; the colour of the gas is hardly visible.	A chloride in presence of a non-volatile oxidising agent such as a chromate or a peroxide.
	Reddish brown fumes are given off.	CrO_2Cl_2 from a chromate and chloride together.
	Reddish brown fumes which bleach moistened litmus paper.	Nitrous fumes and chlorine from a chloride and nitrate together. Or bromine from a bromide.
	Violet fumes. If no oxidising agent other than the H_2SO_4 is present, the Br above is mixed with HBr and SO_2 and the I with H_2S and SO_2.	Iodine from an iodide.
	A greenish yellow gas and detonation in the tube.	Chloric peroxide from a chlorate.
	SO_2 or H_2S or both, recognised by their odour.	A reducing agent that decomposes the sulphuric acid, many sulphides, metals, &c.
	Oxygen is evolved.	From a chromate or peroxide

Experiment.	Observation.	Inference.
If the fumes are colourless and only redden litmus paper, add MnO_2 and strong H_2SO_4 to the substance and warm.	Chlorine is evolved which bleaches litmus paper. In this case nitrates are absent, as if present, chlorine would have been evolved without the addition of MnO_2.	From chlorides.
If nitrates have not already been proved absent, pour strong sulphuric acid on to the substance and carefully float on the top a solution of $FeSO_4$.	A brown layer. Chlorates, bromides, and iodides are likely to interfere with this test. If either is present it is better to dilute the sulphuric acid with an equal bulk of water and cool it before pouring it on the substance. If they are present in considerable quantity they render this test altogether invalid, and nitrates must be looked for subsequently by other means.	Nitrates are present.
If fluorides have been indicated either by the bubbles, when the substance is warmed with H_2SO_4, clinging to the glass, or by evidence of etching already obtained, add sand to the mixture then strong H_2SO_4 and warm, and introduce a wet glass rod into the gas which collects in the tube.	The drops of water are incrusted over, and show a powerful acid reaction when put upon litmus paper. If other acids are given off in large quantity they interfere with this reaction.	Fluorides are present.

THE FINAL EXAMINATION FOR ACID RADICALS.

BEFORE proceeding to this part of the work, it is necessary to review what has already been done, and determine exactly what remains to be done. The analyst has at this stage discovered all the basic radicals present; he has obtained a knowledge of the general character of the substance by the general preliminary examination, and some specific knowledge of the acid radicals present from the results of the preliminary examination for them. The basic radicals present are often evidence of the absence of some of the acid radicals. For example, if barium is present and the substance dissolves in water or dilute acids, no sulphate can be present. The presence of copper, lead, &c., in a readily soluble substance shows that sulphides are absent.

At this stage, therefore, the list of acid radicals specified in the syllabus that the student is working under, should be gone through, and each one considered as to whether it can be present or not. Those that have been proved absent or that cannot be present, and also those that have been conclusively proved to be present, may be passed over. But all those about which any doubt exists should be set down in a list as *the acid radicals that have to be looked for*. The following remarks may assist the student in making this selection.

Carbonates are generally settled conclusively as either present or absent in the preliminary examination, the only exception being when sulphites, sulphides, or nitrites are present. In all cases when an acid radical has to be looked for in the presence of another that interferes with it, reference should be made to the section referring to their reactions in the earlier part of the book. In this case use potassium dichromate instead of hydrochloric acid.

Sulphites, nitrites, chlorates, and *hypochlorites* are also disposed of in the preliminary examination for acid radicals.

Sulphides are proved present or absent in the preliminary examination unless they are not attacked by dilute acids. In this case the sulphide will be insoluble in dilute acids, and can, therefore, as a rule, be easily isolated, and then its character can be determined by attacking it with nitric acid or aqua regia.

The identification of salts of the *sulphur acids* when they occur together in solution has been given in the earlier part of the book in the section on sulphides.

Phosphates need never be further tested for, as they have been proved either present or absent before the separation of Group III.

Silicates have also been tested for, and if present the silica has been separated before Group III., unless they are insoluble, in which case they are found in the examination of the insoluble residue, by the methods given subsequently.

Nitrates are generally finished with in the preliminary examination for acid radicals, but if chlorates, bromides or iodides are present in sufficient quantity, their presence may still be doubtful. In the presence of chlorates, nitrates should be looked for by ignition with sodium carbonate and then testing for nitrites.

Fluorides may still have to be looked for if the test in the preliminary examination has been interfered with by the presence of volatile acids.

Silicofluorides are recognised by their decomposition products, and must, if necessary, be looked for by special methods.

Having made a definite list of acid radicals that have to be looked for, the most suitable solution or preparation for each should be made. Anything known to be present that would interfere with the test to be applied should be got rid of, but things that do not interfere should be allowed to remain. It is unreasonable and detrimental in many ways to make a rule of getting rid of the heavy metals before testing for the acid radicals, and it is also unwise to make a rule of boiling with carbonate of soda for this purpose, because this method is not always effective. Each case must be taken on its own merits, knowing exactly what metals are present and what acid radical it is desired to look for. Of course if several acid radicals have to be looked for that require a similarly prepared solution, then a sufficient amount of the solution may be made for them at once, but this does not often happen.

Sulphates

Prepare a dilute hydrochloric acid extract or solution of the substance, and add $BaCl_2$. A white precipitate insoluble on boiling shows a sulphate to be present.

Silicofluorides give a gelatinous precipitate which cannot be mistaken for barium sulphate. If a silicofluoride is present it can easily be decomposed before testing for sulphates. The metallic radicals do not interfere with this test. If barium or strontium is present they hold this acid radical in the insoluble residue, where it is easily found as described later. By long boiling with sodium carbonate, the sulphates of these metals might be decomposed and sodium sulphate obtained, but this procedure would be disadvantageous rather than otherwise, because it would lead to the confusion of the constituents of the insoluble part with those of the soluble part.

Chlorides

Prepare a dilute nitric acid extract or solution of the substance, and add $AgNO_3$. A white curdy precipitate which is readily soluble in AmOH, shows that a chloride is present. If metals that yield precipitates with AmOH are present, the precipitate should be washed, conveniently by decantation, before adding the AmOH.

If silver is present, silver chloride will remain in the insoluble residue, and be there recognised. A mercurous salt might prevent this reaction; when present, therefore, it is well to add a drop or two of strong nitric acid to the substance, and to warm it to oxidise the mercurous salt, then to add water, filter if necessary, and test as above.

This test for chlorides must be modified if a bromide or iodide is present, as stated below. If the silver precipitate is dissolved easily by AmOH, this proves the absence of bromides and iodides.

Chlorides, Bromides, Iodides, and Nitrates

If either a bromide or an iodide is present, then these three halogens must be specially tested for, and it is often convenient to look for nitrates at the same time.

First, test for or confirm the presence of iodides, by adding some starch paste to the original substance and chlorine water a drop at a time. If an iodide is present the characteristic blue colour will be produced. If not present, proceed as given below as if it had been present and removed.

If iodides are present, the iodine must be removed. (If metals are present that form bromides insoluble in dilute acids ($AgBr$, Hg_2Br_2, $PbBr_2$), these bromides will be left insoluble by the following treatment, and are best attacked as stated in the section on insoluble residues.)   To a dilute HNO_3 extract or solution, add H_2SO_3 and $CuSO_4$, warm, and filter off the nearly white Cu_2I_2. Boil the solution to get rid of SO_2.

To test for bromides and chlorides, divide the filtrate into two parts. To one add CS_2 or chloroform, and chlorine water or $NaOCl$ a drop at a time and shake. The CS_2 or chloroform is coloured brown if bromides are present. The other part of the solution, if bromides are absent, test as usual for chlorides. If bromides are present precipitate completely with silver nitrate, wash the precipitate by decantation, pour water over it to about a third fill the test tube, add about from 5 to 10 drops of dilute ammonia, shake, and filter. To the filtrate add HNO_3, and a white precipitate easily soluble in AmOH shows that chlorides were present.

Another method of testing for chlorides, is to get rid of the bromine and iodine by boiling a solution well acidified with dilute H_2SO_4 and adding a solution of $K_2Mn_2O_8$ during the boiling until a drop gives a pink tint to the whole liquid. The boiling must be continued further for about half a minute to get rid of the last parts of the bromine. The solution is then cooled and tested as usual for chlorides. An appreciable quantity of chlorine is easily detected by this method, but a small quantity is always lost.

Nitrates may be conveniently tested for in a part of the solution that has been thus freed from iodine and bromine.

Fluorides

If other matters interfere with the detection of these salts at once, the fluoride must be separated from them. If a chloride interferes, water may dissolve away the chloride and leave the fluoride. If the fluoride dissolves too in water, $CaCl_2$ may be added when CaF_2 will be precipitated. In any case the fluoride when

obtained free from interfering substances must be examined by its action on silica (or glass), either by getting SiF_4 which deposits hydrated silica on coming into contact with water, or by the etching of glass. $Ca_3P_2O_8$ and $CaSO_4$, which may be precipitated with the fluoride, do not interfere with these tests.

Borates

To the solid substance add about half its bulk of CaF_2, and make the whole into a paste with strong H_2SO_4. Fill a platinum wire loop with the paste, hold it near to the Bunsen flame, and look for a green colour in the flame. Much copper will make the test uncertain if only a small quantity of boric acid is present. To get rid of it, make a dilute hydrochloric acid extract or solution of the substance, pass H_2S, filter off the CuS, add enough Na_2CO_3 to neutralise the acid, evaporate to dryness and test the residue as above.

THE SUMMARY AND GENERAL REMARKS

THE constituents found are now to be clearly stated, the basic radicals first and then the acid radicals. Care must be taken that chromium is properly classed, and not set down as a basic radical unless it really exists as such in the substance. Of course chromium, however present, is found in Group III, but the question is not the condition that the analyst has brought the chromium into, but the condition in which it existed in the substance given.

After the statement of the constituents found, a short section headed "General Remarks" should follow. It is sometimes possible to tell exactly what substances were present, and not merely the acid and basic radicals. For example, if a mixture of ferric oxide and sodium chloride were given, the absence of deliquescence would show at once that the iron was as oxide and not as chloride, and the fact that none of the iron was soluble in water, would further prove this. The water extract would be colourless and neutral to litmus, and this would show that the sodium was not present as oxide or hydrate. Putting these facts together, it will be seen that it is impossible in this case for the iron, sodium and chlorine to exist together in any other way than as sodium chloride and ferric oxide.

It seldom happens, however, that the compounds present can be exactly demon-strated. Suppose, for example, a yellow powder that contains chlorides, chromates, lead, ammonium and potassium. In accounting for the yellow colour it would be necessary to give all the substances that are yellow and might be present, namely, lead, ammonium, and potassium chromates, and lead oxide. To suggest that the powder was a mixture of lead chromate and potassium chloride and ammonium chloride would be to make a mere guess, and guesses are entirely out of place. No inference of any kind must be made unless it is fully supported by observations. In this case, if the whole of the lead and the chromium were left insoluble on

adding water, even then it would not be proved that the lead was present in the powder as lead chromate, because it is possible that exactly the required amount of potassium or ammonium chromate had been used to transform the whole of the lead into chromate.

In making these general remarks there are two items that can always be included, namely, the *colour* and the *solubility;* and the *reaction* of the aqueous extract to litmus paper can always be added when any part of the substance is soluble in water. There are comparatively few cases where a metal is present as an *oxide* and the fact cannot be proved. These, therefore, are matters to which attention should at first be paid, and then should follow any other observations of an analogous character with the inferences that can be properly drawn from them.

If these general remarks are lengthy, a second summary may well be given; but if short, they may remain as an appendix to the work.

AN EXAMPLE ANALYSIS

THE substance consisted of a mixture of AmCl, KNO_3, $MgSO_4,7H_2O$, and Fe_2O_3.

In notes of work such as this, words may and should be contracted where possible, but all contractions must be intelligible. If in doubt write the word in full. When a constituent is proved present, it is a good plan to underline it, so that it may not be missed in looking over the notes.

EXAM. OF A LIGHT RED POWDER.

Prelim. Exam.

1. Heated in a bulb-tube.	Fused. Gave off	
	H_2O.	H_2O.
	odour of NH_3.	Am.
	white sublimate.	Am, Hg, As, &c.
	red fumes (acid to litmus).	Nitrates.
	Residue	
	red (dark brown hot).	Fe_2O_3.
	infusible.	
Ground with soda-lime.	Odour of NH_3 (blueing litmus).	Am present.
2. Heated on charcoal.	Deflagration.	Nitrates, chlorates.
	Red infusible residue.	Fe_2O_3.
Heated on a borax bead.	Outer flame — yellow, inner flame — bottle green.	Fe.
3. Heated on a platinum wire.	Flame coloured feeble yellow, then violet.	K.

O

Exam. of Sol. for Basic Radicals.

Part sol. in H_2O and neutral to litmus.   Residue red and sol. in HCl.

Disd. in dil. HCl.   Sol. is yellow.

No ppt. Grp. 1 abst.	Sol. Passed H_2S through a few drops.			
	Wht. ppt. S only. Grp. 2 abst.	Sol. (remainder). To a few drops added HNO_3 and Am_2MoO_4 and warmed. No ppt. Phosphates absent. Added AmCl, boiled, added AmOH.		
		Red ppt. Grp. 3A prest.	Sol. Passed H_2S.	
			No ppt. Grp. 3B abst.	Sol. Added Am_2CO_3.
				No ppt. Grp. 4 abst.	Sol. Grp. 5

Exam. of Ppt. produced for Group III.a.

Disd. in HCl, sol. is yellow, added NaOH in excess.

Red ppt. Fused with fusion mixture and KNO₃, extracted with H_2O.		Sol. Added HCl and AmOH. No ppt. Al abst.
Red residue. Disd. in dil. HCl. Added K_4FeCy_6. Dark bue ppt. Fe prest.	Sol. colourless. Added acetic acid and $Pb(C_2H_3O_2)_2$. No ppt. Cr abst.	

Exam. of Sol. for Group V.

Divided.

| 1.
Added HNa_2PO_4
wht. ppt.
<u>Mg prest.</u> | 2.
Evapd. to dryness, ignited. Heated on platinum wire.
    Violet flame. Na abst. <u>K prest.</u>
    Disd. in H_2O, added $PtCl_4$, evapd. just to dryness, added alcohol.
    Yellow crystalline ppt. <u>K prest.</u> |

Tests for ferrous and ferric iron.

Disd. in HCl, added $K_6Fe_2Cy_{12}$. A brown colour, no ppt. Fe″ abst.
Disd. in HCl, added AmCyS. A deep red colour. <u>Fe‴ prest.</u>

Prelim. Exam. for Acid Radicals.

1. Warmed with dil. HCl.	No gas evolved.	Carbonates, sulphites, &c., abst.
2. Warmed with strong H_2SO_4.	Reddish brown fumes, bleaching litmus paper.	Chlorides and nitrates, or bromides.
Added strong H_2SO_4 and $FeSO_4$.	Brown layer where the liquids meet.	<u>Nitrates prest.</u>

Final Exam. for Acid Radicals.

To be looked for. Sulphates, chlorates, borates.

Disd. in dil. HCl, added $BaCl_2$, wht. pp. insol. on boiling. <u>Sulphates prest.</u>

Extracted with dil. HNO_3, added $AgNO_3$, wht. curdy ppt. sol. in AmOH. <u>Chlorides prest.</u>

Made a paste with the substance, CaF_2, and strong H_2SO_4, and heated on platinum wire. Flame is not coloured green. Borates abst.

<div align="center">

Found :—Basic radicals, Am . Fe . Mg . K.
Acid radicals, NO_3 . SO_4 . Cl.

</div>

General Remarks

The substance is light red.	Fe_2O_3 and Fe_2Cl_6 are reddish.
The aqueous extract is neutral and colourless.	Fe_2Cl_6, KOH and MgO absent. The nitrates, chlorides and sulphates of Am, K and Mg are soluble in water, give colourless solutions, and are neutral.
The part insol. is H_2O is red and sol. in HCl.	Fe_2O_3 is insol. in H_2O, red and sol. in HCl.

Therefore the iron is present as Fe_2O_3 and the other metals as neutral salts.

INSOLUBLE SUBSTANCES OR RESIDUES

It is impossible to give a complete list of insoluble substances, but for most purposes the following will serve as a guide.

Silica and many silicates (some including potassium and sodium silicates, as glass, felspar, &c.).

Sulphates of barium and strontium (calcium sulphate dissolves only tardily and in much bulk of dilute acid).

Silver chloride, bromide and iodide.

Tin dioxide.

Calcium fluoride and a few other fluorides.

Alumina (as corundum, sapphire, ruby, &c. Artificial alumina after very intense ignition is also insoluble).

Sulphur.

Carbon.

Chrome iron ore, and some mineral phosphates and arsenates.

Some other oxides, such as those of iron, chromium, and antimony, by ignition at a very high temperature may be made difficult to dissolve if not insoluble.

Many of these substances give reactions in the preliminary examination, especially the tin and silver compounds, sulphur and carbon. Sulphur is separated by its volatility when heated or its solubility in carbon disulphide. Carbon is recognised by its black colour and its deflagration when heated with potassium nitrate.

Many other substances that are black, such as manganese dioxide and copper oxide, are not insoluble.

The silver haloid compounds can be dissolved out with a solution of potassium cyanide, and ammonium sulphide will give a black precipitate of silver sulphide when added to the solution. Silver chloride is easily dissolved in ammonia, reprecipitated by acidification, and so recognised. But any of these compounds may be decomposed by dilute sulphuric acid and zinc put so that it touches the mass. The halogen dissolves in combination with the zinc, and metallic silver remains. This decomposition may require some hours for completion; but from ten to twenty minutes may be relied on to give enough of the halogen in solution for identification.

Calcium fluoride may generally be suspected if present by the recognition of the presence of fluorides in the ordinary examination for acid radicals, and the precipitation of a little calcium fluoride with ammonia in Group III., and also perhaps by the etching when heated in the bulb-tube.

The Examination

The insoluble part should be thoroughly washed with hot water, especially if lead is present in the substance. If the analyst is not confident of the absence of silver, a small part should be treated with potassium cyanide and tested as stated above. If, however, aqua regia has been used in removing the soluble part, any silver iodide or bromide will be changed into chloride, and the chloride may be removed by dissolving it out in ammonia. This method is to be recommended for removing the silver. The identification of bromine and iodine when in combination with silver, is conveniently effected by the action of zinc and sulphuric acid, as given above, on a part of

the insoluble residue obtained without the use of aqua regia.

In the absence of silver, or after having removed it, the insoluble residue should be fused with about six times its bulk of fusion mixture on platinum foil. If the insoluble residue contains compounds of chromium or of any easily reducible metal such as tin, a little nitrate of potassium may be added, otherwise it is as well to omit it. The fused mass is warmed with water until thoroughly disintegrated, filtered, and the residue well washed.

The residue is dissolved in hydrochloric acid and examined in the usual manner for basic radicals, except of course potassium and sodium.

The aqueous extract is examined in separate portions (1) for the acid radicals that might form insoluble compounds with the basic radicals found, (2) for the heavy metals, especially those of Group II. (tin in particular), and (3) also for silica. The examination for silica should be carried out by acidification of a part with hydrochloric acid, evaporation to dryness and treatment of the residue with hydrochloric acid and water, looking for the insoluble silica. It is not impossible that some silica may be left in the residue insoluble in water after fusion, but it is hardly possible for it all to be there. It is therefore generally sufficient to examine for silica in the aqueous extract.

Calcium fluoride will be only partially decomposed by the fusion unless silica is also present, but it is sufficiently acted on in any case to allow of the detection of its constituents. The undecomposed part will dissolve at least partially in hydrochloric acid, and gives a white precipitate with ammonia which does not dissolve in excess of caustic soda.

Aluminium phosphate occurring in minerals such as wavellite, also is not decomposed by fusion with alkaline

carbonates only.   To effect its decomposition, it is fused as directed above, but adding rather more than as much silica as of the mineral.   After digesting the mass with water until it is disintegrated, ammonium carbonate is added and the digestion is continued to precipitate the silica and alumina, and then the mixture is filtered.   The phosphorus is in the solution as alkaline phosphate.   The residue containing the metals as oxides or carbonates with the silica is examined without further difficulty.

Minerals may contain potassium or sodium, and obviously these metals could not be identified after fusion with the alkaline carbonates.   It is possible to attack some silicates and fluorides that are but little if at all affected by hydrochloric acid, by the action of strong sulphuric acid.   Silicates may also be decomposed by heating them with solid barium hydrate, or by hydrofluoric acid, but the best method of attacking them in order to search for alkalies is that given in the section on Silicates, by the use of calcium carbonate and ammonium chloride.

METALS AND ALLOYS

A metal or alloy can generally be identified as such at once by mere inspection.   It is nevertheless not desirable to omit the preliminary examination.   Heating in the bulb-tube will effect the fusion of many of them; some, such as mercury, cadmium and arsenic may give a sublimate; others, such as brass or copper, will show changes due to oxidation, and so may be distinguished from non-oxidisable metallic substances.   Heating on charcoal will give further information perhaps as to fusibility, and may give incrustations from the more volatile constituents.

Metals that dissolve readily in hydrochloric acid, such as zinc and cadmium when not too pure, may be so dissolved,

but in by far the greater number of cases it is best to use nitric acid. The alloy should if possible be powdered either by filing or pounding (if brittle), though pieces of considerable size can be attacked if sufficient time is allowed. The nitric acid should be a little diluted, with say half its bulk of water, or a little water may be added first and then strong nitric acid. When the vigour of the reaction slackens, the mixture should be heated and finally well boiled until the attack is complete and a little longer. Water is then added and the solution again boiled.

A metallic powder remaining insoluble that is soluble in aqua regia generally indicates gold or platinum, or a similar metal. Tin and antimony give white residues of the oxides (or hydrated oxides). Such a residue is well washed and boiled with a strong solution of tartaric acid. The antimony oxide dissolves and the sulphide may be precipitated and identified as usual. The metastannic acid remains unattacked by the tartaric acid, and after washing may be reduced to the metallic state by heating it either on charcoal with fusion mixture and potassium cyanide, or in a porcelain crucible by using the cyanide alone. A large excess of the flux should be used, and a porcelain crucible will be attacked somewhat. The metallic tin may then be hammered flat, dissolved in strong hydrochloric acid, putting in a piece of platinum foil or wire to assist the solution, and the resulting stannous chloride identified as usual.

The nitric acid solution is to be examined for metals in the ordinary manner. If antimony was present, a little of it will be found in this solution, but tin should be entirely left in the residue.

In examining metals and alloys, the search for the acid radicals may be omitted. Some metallic substances contain small quantities of non-metallic elements, such as carbon, sulphur and phosphorus, but the special methods

employed in the examination for these in metals does not come within the scope of this volume.

THE SUBSTANCE GIVEN FOR EXAMINATION IS A SOLUTION

The solution should first be examined as to its colour and odour, and its reaction to litmus. Such substances as ammonia, sulphurous anhydride, sulphuretted hydrogen, iodine, bromine and chlorine are recognised at once and easily confirmed. The ordinary acids, hydrochloric, nitric and sulphuric, will also be readily distinguished. If then by evaporation at a gentle heat there is no residue, it only remains to confirm the presence of the substances indicated, bearing in mind that there may be more than one. There may be, for example, a mixture of bromine and chlorine dissolved in water.

If the liquid has no obvious properties that lead to the suspected presence of such substances as those just mentioned, and it is alkaline to litmus, a portion should be acidified with hydrochloric acid, preparatory to the ordinary examination for basic radicals.. This may cause the evolution of a gas, such as carbonic or sulphurous anhydride or sulphuretted hydrogen ; if so, the gas must be identified. It may precipitate such substances as lead chromate or sulphate from their solutions in caustic alkalies, the sulphides of tin, arsenic, and antimony from the solution of them in alkalies or alkaline sulphides, sulphur from a polysulphide, hydrated silica from an alkaline silicate, alumina or aluminium phosphate from its solution in caustic soda or potash, boric acid from a borate, and perhaps a few other substances. These precipitates are generally so characteristic in their appearance, or are so easily identified by simple means, that it would be waste of time to attempt to devise a single

scheme of examination that should detect all of them. If the precipitate is easily soluble on adding more acid, as alumina is, it should be dissolved, and the solution is ready for examination for basic radicals in the usual manner. If not soluble, it is filtered off and examined by itself, and the solution is also examined for basic radicals.

It is sometimes perhaps worth while to evaporate a part of the solution to dryness and subject the residue to the ordinary preliminary examination ; but in most cases this is not desirable. Ammonium, unless certainly absent, should be tested for in a part of the original solution.

In looking for the acid radicals, every one that can possibly be present must be considered. To test for borates, a slight excess of sodium carbonate should be added, if the liquid is acid, and a few drops evaporated to dryness for testing with fluor spar and sulphuric acid in the flame.

REAGENTS

THE reagents that are required for analytical work can generally be obtained without trouble in a fit condition. In the case of those of which more than one quality is sold, unless otherwise stated the commercial " pure " preparation should be obtained. It must be understood that the few tests given are not always sufficient to prove the suitability of the substance, but they indicate the most likely sources of failure if the reagent is at fault.

Water should be distilled, except in those parts of the country where the ordinary supply is sufficiently pure. It should give no turbidity with ammonium oxalate, silver nitrate, or barium chloride, and leave no residue on evaporation.

Alcohol. Methylated spirit is sufficient if that kind can be obtained that does not become turbid when water is added to it.

Ether. Any ordinary sample as purchased.

Carbon Disulphide or *Chloroform.* The ordinary commercial preparations.

Hydrochloric acid should be " pure." S.G. 1·16 is sufficient. It should not be kept in a strong light, or a little of it will be decomposed, giving free chlorine. Chlorine may be tested for by adding about an equal bulk of water, and a little potassium iodide and starch.

A blue colour due to the liberation of iodine shows that chlorine is present.

Dilute hydrochloric acid is prepared by adding three times its bulk of water to the above.

Nitric acid should be " pure." S.G. 1·36 is sufficient.

Dilute nitric acid is prepared by adding three times its bulk of water to the above.

Sulphuric acid may be the ordinary commercial acid if a fairly colourless sample that gives no reaction for nitric acid can be obtained. It must be noted that it always contains lead. For some special experiments a purer acid may be needed, then the commercial " pure " quality should be obtained.

Dilute sulphuric acid is prepared by slowly pouring a measured quantity of the above into five times its bulk of water, with constant stirring. A white precipitate of lead sulphate will be obtained which should be allowed to settle, and the clear liquid may then be decanted off.

Acetic Acid. That described as " Fort. B.P." is suitable, and may be diluted with an equal bulk of water.

Tartaric acid is prepared as a saturated solution, but only in small quantities at a time as its solution decomposes.

Hydrofluosilicic Acid, if to be used for precipitating barium, should be free enough from sulphuric acid not to give a precipitate with a strontium salt.

Sulphurous acid should be kept in small bottles, as it rapidly loses sulphurous anhydride when exposed.

Chlorine water should also be kept in a small bottle that is frequently refilled, and should not be exposed to a strong light as it stands on the shelf, as light causes the chlorine to react with the water forming hydrochloric acid and oxygen.

Bromine water is prepared by pouring a few cubic

centimetres of bromine into a bottle of convenient size nearly full of water and shaking a little. If all the bromine dissolves, some more should be added.

Potassium iodide is dissolved in forty times its weight of water, giving about a $2\frac{1}{2}$ °/₀ solution.

Potassium chromate is prepared as a 10 °/₀ solution—that is, 10 grams is dissolved and the bulk made up to 100 cc. It should give no precipitate with barium chloride that does not completely dissolve in dilute hydrochloric acid.

Potassium Pyroantimonate (commonly called *Metantimonate*). A 5 °/₀ solution is prepared.

Potassium ferrocyanide is dissolved in twelve times its weight of water.

Potassium ferricyanide is always wanted in solution, but it is best kept in the solid state, a crystal or two being washed and dissolved as required. The solution is speedily partially reduced to ferrocyanide, and is then useless.

Potassium or *ammonium thiocyanate* is dissolved to form a 10 °/₀ solution.

Ammonia. The strongest " liquor ammoniæ " is diluted with three times its bulk of water. It should give no precipitate with barium chloride.

Ammonium chloride is dissolved to a 20 °/₀ solution and allowed to settle. The clear solution is decanted off.

Ammonium sulphide as purchased is mixed with rather less than its own bulk of strong ammonia and about eight times its bulk of water.

Ammonium Carbonate. The ordinary preparation is dissolved in four times its weight of water, and its own weight of strong ammonia is added.

Hydrogen Ammonium Carbonate. A saturated solution is prepared without heating.

Ammonium Molybdate. Dissolve 16 grams of the salt in a mixture of 20 cc. of strong ammonia and 20 cc. of water.

If a precipitate appears on standing, allow it to subside. Make a mixture of 75 cc. of strong nitric acid with 75 cc. of water, and to this add slowly the ammonia solution of the salt, stirring all the time that the white precipitate that appears at first may redissolve in the acid. The preparation may be diluted with 100 cc. of water. The solution should give no precipitate when warmed.

Ammonium Oxalate. A 5 °/₀ solution is prepared.

Ammonium Sulphate. A saturated solution is prepared.

Sodium Hydrate or *Caustic Soda.* This can now be obtained in a powdered state and of excellent quality. Of the small proportion of foreign matter, much is insoluble in water. A 5 °/₀ solution is prepared, the insoluble matter is allowed to settle down, and the clear solution is decanted off.

Sodium Hydrogen Phosphate. A 10 °/₀ solution is prepared.

Sodium Carbonate. A 20 °/₀ solution of the pure crystalline salt is prepared.

Sodium Acetate. A 10 °/₀ solution is prepared.

Sodium Acetate and Acetic Acid. Dissolve 20 grams of sodium acetate in 160 cc. of water, and add 40 cc. of undiluted acetic acid.

Sodium hypochlorite may be used as purchased.

Barium Hydrate. Shake up the crystals in a stoppered bottle with about 20 times their weight of water. Allow to settle, and decant.

Barium Chloride. Prepare a 10 °/₀ solution.

Barium carbonate is best kept for use as a rather thick milky mixture with water. It is better to prepare the carbonate by precipitating a solution of barium chloride with ammonium carbonate, and thoroughly washing the precipitate, than to obtain the carbonate ready made.

Calcium Hydrate or *Lime Water.* Shake up slaked

lime in a bottle of water, allow to subside, and decant or filter off the clear solution.

Calcium Chloride. Prepare a 10 °/₀ solution of the crystals.

Calcium Sulphate. Shake up the powdered salt with water, allow to subside, and decant or filter.

Magnesium Sulphate. Prepare a 10 °/₀ solution.

Magnesia Mixture. Dissolve 55 grams of crystallised magnesium chloride and 70 grams of ammonium chloride in water, add 350 cc. of strong ammonia, and make up the total bulk to one litre.

Ferrous Sulphate. Prepare a 10 °/₀ solution. It is advisable to add about two drops of strong sulphuric acid to each litre of water before dissolving the salt in it.

Ferric Chloride. Prepare a 10 °/₀ solution.

Lead Acetate. Prepare a 10 °/₀ solution, adding two or three cc. of acetic acid to each litre of water used before dissolving the salt.

Silver Nitrate. Prepare a 5 °/₀ solution.

Mercuric Chloride. Prepare a 5 °/₀ or saturated solution.

Nessler's Solution. Dissolve 3·5 grams of potassium iodide in 10 cc. of water, and add to it the above solution of mercuric chloride until the precipitate produced just ceases to dissolve on agitation. Add about 60 cc. of caustic soda solution, and allow the mixture to stand in a closed bottle. Decant off for use.

Copper Sulphate. Prepare a 10 °/₀ solution.

Stannous Chloride. Dissolve the crystals in a quantity of strong hydrochloric acid that is not much more than sufficient to cover them, and add 8 to 10 times the bulk of water. A little metallic tin should be kept in the solution.

Auric Chloride. The contents of a 15 grain tube may be dissolved in about 50 cc. of water.

Platinic Chloride. Prepare a 5 °/₀ solution.

Cobalt Nitrate. Prepare a 10 °/₀ solution.

Indigo Solution. Indigo sulphate solution may be used as purchased.

Litmus Extract. Powder two or three grams of litmus, and warm gently with 100 cc. of water until the residue is nearly white, and filter the extract.

DRY REAGENTS

Sodium Carbonate, anhydrous. It should be free from chlorides and sulphates, especially the latter.

Fusion mixture may be prepared by intimately grinding together 10 parts by weight of dry sodium carbonate, and 13 parts by weight of dry potassium carbonate.

Potassium Cyanide. The 30 °/₀ is good enough as a flux. A solution of it will also serve for the reactions in solution, though for this a superior quality is to be preferred. The solution of this salt must be made as wanted, because it will not keep long without decomposition.

Potassium Nitrate. As purchased.

Potassium Dichromate. As purchased.

Potassium Chlorate. As purchased.

Potassium Ferricyanide. The use of this has been described above. It is kept in the solid state because its solution is not stable under ordinary circumstances.

Borax. The calcined is preferable.

Lead Dioxide. As purchased. For use it may be shaken up with water to a creamy consistency ; but this is of very little advantage.

Manganese Dioxide. The powdered mineral, pyrolusite. It should not give off any chlorine when warmed with strong sulphuric acid.

ATOMIC WEIGHTS

In this table the first figure in each case is the atomic weight deduced from the most reliable experimental data available, and the second figure where given is a simpler one that is sufficiently near for all the calculations for which the student may require atomic weights. (The atomic weights are those given by Ostwald in his *Outlines of General Chemistry*, where further information may be obtained respecting them. Oxygen is taken as 16.)

NAME.	SYMBOL.	ATOMIC WEIGHT.	
Aluminium	Al	27·08	27
Antimony	Sb	120·3	120
Arsenic	As	75·0	75
Barium	Ba	137·0	137
Beryllium	Be	9·10	
Bismuth	Bi	208·0	208
Boron	B	11·01	11
Bromine	Br	79·963	80
Cadmium	Cd	112·1	112
Cæsium	Cs	132·9	
Calcium	Ca	40·0	40
Carbon	C	12·00	12
Cerium	Ce	140·2	
Chlorine	Cl	35·453	35·5
Chromium	Cr	52·2	52·2
Cobalt	Co	59 (?)	59
Copper	Cu	63·3	63·3
Didymium		(?)	
Erbium	Er	166	
Fluorine	F	19·0	19
Gallium	Ga	69·9	
Germanium	Ge	72·3	
Gold	Au	197·2	197
Hydrogen	H	1·003	1
Indium	In	113·7	
Iodine	I	126·86	127
Iridium	Ir	193·2	
Iron	Fe	56·0	56
Lanthanum	La	138·5	

Name.	Symbol.	Atomic Weight.	
Lead	Pb	206·91	207
Lithium	Li	7·03	
Magnesium	Mg	24·38	24·4
Manganese	Mn	55·0	55
Mercury	Hg	200·4	200
Molybdenum	Mo	95·9	
Nickel.	Ni	59 (?)	59
Niobium	Nb	94·2	
Nitrogen	N	14·041	14
Osmium	Os	192	
Oxygen	O	16	16
Palladium	Pd	106	
Phosphorus	P	31·03	31
Platinum.	Pt	194·8	195
Potassium	K	39·14	39
Rhodium	Rh	103	
Rubidium	Rb	85·4	
Ruthenium	Ru	101·7	
Samarium	Sm	150	
Scandium	Sc	44·1	
Selenium	Se	79·1	
Silicon	Si	28·4	28·4
Silver	Ag	107·938	108
Sodium	Na	23·06	23
Strontium	Sr	87·5	87·5
Sulphur	S	32·06	32
Tantalum.	Ta	183	
Tellurium	Te	125	
Thallium	Tl	204·1	
Thorium	Th	232·4	
Thulium	Tu	171	
Tin	Sn	118·1	118
Titanium	Ti	48·1	
Tungsten	W	184·0	
Uranium	U	239·4	
Vanadium	V	51·2	
Ytterbium	Yb	173·2	
Yttrium	Y	88·7	
Zinc	Zn	65·5	65·5
Zirconium	Zr	90·7	

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